

For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAENSIS



THE UNIVERSITY OF ALBERTA

PHOTOLYSIS OF ALKYL-PYRAZOLINES

BY

(C)

RALPH BISHOP MOORE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

AUGUST 1967

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled PHOTOLYSIS OF ALKYL-PYRAZOLINES submitted by Ralph Bishop Moore, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ACKNOWLEDGMENTS

The author would like to express his sincere appreciation to Dr. R. J. Crawford, whose ideas and guidance were a constant source of inspiration throughout the course of this work.

He would also like to thank the staff of the spectroscopy laboratory, who so cheerfully performed the nmr and ir spectra.

To his wife, Colette, who performed much of the typing, and whose encouragement was always appreciated, he is especially indebted.

Finally, the author wishes to express his gratitude to the University of Alberta for providing him with generous financial help in the form of Graduate Teaching Assistantships throughout the course of his study.

ABSTRACT

The gas phase thermolysis of simple alkyl substituted pyrazolines has been proposed to proceed through a trimethylene intermediate. Furthermore, this intermediate could potentially be the same type which has been proposed to arise in cyclopropane thermolysis and methylene addition to olefins. With this in mind, seven simple pyrazolines have been photolyzed in the gas phase and five of them also decomposed in solution by both direct photolysis and benzophenone photosensitization. The photolyses would presumably produce a trimethylene intermediate of higher energy content than that produced thermally.

At low pressures, the initially formed cyclopropanes were found to undergo isomerization to olefins. From the pressure dependence of this isomerization, an estimation of the excess energy content of the cyclopropane initially formed in 1-pyrazoline photolysis was made. A value of approximately 90 kcal/mole was determined, which is considerably lower than the values obtained for the cyclopropane formed in the addition of methylene to ethylene.

The 1,2-dimethylcyclopropanes formed from the direct photolysis of 3,5-dimethyl-1-pyrazoline do not exhibit stereoselectivity to the same extent as those produced in the thermolysis process, which is in accord with the intermediate having a higher energy content in the photolysis process. The photosensitized decomposition of the four dimethyl-pyrazolines studied produced a mixture of cis- and trans-1,2-dimethylcyclopropane which lay near the equilibrium value in all cases. This probably reflects

a longer lifetime for the intermediate compared to that produced in direct photolysis.

The olefins produced from 3-methyl- and 4-methyl-1-pyrazoline lend support to the idea that cyclopropane thermolysis proceeds through a trimethylene intermediate, while the addition of methylene (singlet) to olefins does not. The olefins produced from the direct photolysis of 3,4-dimethyl-1-pyrazoline also support this idea by virtue of the fact that 2-methyl-1-butene is always produced from 3,4-dimethyl-1-pyrazoline decomposition, while in the addition of singlet methylene to 2-butene, at high pressures, 2-methyl-1-butene is not observed. The pentenes produced from the direct photolysis of 3,5-dimethyl-1-pyrazoline support theoretical predictions that states other than the ground state singlet of the trimethylene intermediate will be 'floppy' molecules.

The photosensitized decomposition of the disubstituted pyrazolines produces very little olefin, and in particular, no olefin arising from a 1,4-hydrogen migration in the triplet intermediate. This type of hydrogen migration has been proposed to account for the appearance of 3-methyl-1-butene in the addition of triplet methylene to 2-butene. It therefore appears that the 3-methyl-1-butene arises from some alternate mechanism in this latter reaction.

In all the pyrazolines studied, products (olefins) resulting from carbon-carbon bond fission appeared. From the stereochemistry of these products a concerted retro-1,3-dipolar addition mechanism is favored for this process.

PART II

By analogy with 1-pyrazoline decomposition 3,4,5,6-tetrahydropyridazine is a possible source of tetramethylene diradicals. An attempt was made to prepare 3,4,5,6-tetrahydropyridazine, but difficulty arose when it was found that it tautomerized very rapidly to the cyclic hydrazine, 1,4,5,6-tetrahydropyridazine.

Tautomerizations of azo compounds have been observed in the past, and it was decided to try and obtain kinetic data on the base catalyzed tautomerization of 3,4,5,6-tetrahydropyridazine and compare it with the tautomerization data of 1-pyrazoline and azoethane.

It was found that the tautomerization was first order in base catalyst and first order in azo compound. The rate for 3,4,5,6-tetrahydropyridazine was found to be about one hundred to one hundred and fifty times faster than the tautomerization rate of 1-pyrazoline, and one to two thousand times faster than the rate for azoethane. All the reactions were characterized by large negative entropies of activation.

The mechanism proposed for the tautomerization is similar to that put forward for the base catalyzed tautomerization of olefins involving the abstraction of an allylic proton by the base followed by shift of the double bond.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	iii
ABSTRACT	iv
LIST OF TABLES	ix
LIST OF FIGURES AND SCHEMES	xi
<u>CHAPTER I</u> <u>Historical</u>	1
(a) Cyclopropane Thermolysis	2
(b) Methylene Addition to Olefins	10
(c) Pyrazoline Decompositions	29
(d) Cyclobutanone Photolysis	40
(e) Theoretical Treatment of Trimethylene	40
<u>CHAPTER II</u> <u>Proposal</u>	43
<u>CHAPTER III</u> <u>Results and Discussion</u>	46
(A) Results	46
Excess Energy of Cyclopropane	60
(B) Discussion	63
(a) Energy Content of Cyclopropane	63
(b) Cyclopropane Forming Reactions	65
(c) Olefin Forming Reactions	69
(d) Cleavage Reactions	80
SUMMARY	84

LIST OF TABLES

	<u>Page</u>
TABLE 1 Dimethylcyclopropane Thermolysis Products	8
TABLE 2 Methylene Addition to 2-Butene	11
TABLE 3 Methylene Addition to Cyclopropane and Propylene	14
TABLE 4 Olefins from "Hot" Methylcyclopropanes	15
TABLE 5 Methylene Addition to 2-Butene	17
TABLE 6 Methylene Addition to <u>cis</u> -2-Butene	19
TABLE 7 Triplet Methylene Addition to <u>cis</u> -2-Butene	21
TABLE 8 Triplet Methylene Addition to <u>cis</u> -2-Butene	22
TABLE 9 Triplet Methylene Addition to <u>cis</u> -2-Butene (Mercury Photosensitized)	27
TABLE 10 Thermolysis Products of 1-Pyrazolines	31
TABLE 11 Photolysis of 1-Pyrazoline	47
TABLE 12 Photolysis of 3-Methyl- and 4-Methyl-1-Pyrazoline	50
TABLE 13 Gas Phase Photolysis of <u>trans</u> -3,5-Dimethyl-1- Pyrazoline	51
TABLE 14 Liquid Phase Photolysis of <u>trans</u> -3,5-Dimethyl-1- Pyrazoline	52
TABLE 15 Gas Phase Photolysis of <u>cis</u> -3,5-Dimethyl-1-Pyrazoline	53
TABLE 16 Liquid Phase Photolysis of <u>cis</u> -3,5-Dimethyl-1- Pyrazoline	54
TABLE 17 Total Product Yields for <u>cis</u> - and <u>trans</u> -3,5-Dimethyl- 1-Pyrazoline Photolysis	55
TABLE 18 Gas Phase Photolysis of <u>trans</u> -3,4-Dimethyl-1- Pyrazoline	56

Page

TABLE 19	Liquid Phase Photolysis of <u>trans</u> -3,4-Dimethyl-1-Pyrazoline	57
TABLE 20	Gas Phase Photolysis of <u>cis</u> -3,4-Dimethyl-1-Pyrazoline	58
TABLE 21	Liquid Phase Photolysis of <u>cis</u> -3,4-Dimethyl-1-Pyrazoline	59
TABLE 22	Relative Butene Yields from Various Sources	72
TABLE 23	Reference Hydrocarbons for gc	88
TABLE 24	Retention Times for Silver Nitrate - Tris (2-cyanoethoxy)-propane Column	92
TABLE 25	Retention Data for Silver Nitrate Dimethylsulfolane Column	93
TABLE 26	Product Loss on Trapping from gc	99
TABLE 27	Hydrocarbon Loss on Trapping from gc	101
TABLE 28	Undetected Products in Liquid Phase Pyrazoline Photolysis	103

LIST OF FIGURES

		<u>Page</u>
FIGURE 1	Energy Profile Diagram for 1-Pyrazoline Photolysis	62
FIGURE 2	Configuration of Intermediate from 3-Methyl- 1-Pyrazoline	73
FIGURE 3	Configurations of the Intermediate from <u>cis</u> - and <u>trans</u> -3,4-Dimethyl-1-Pyrazoline	79
FIGURE 4	Vacuum Apparatus	90
FIGURE 5	Bulb Crusher	91

LIST OF SCHEMES

SCHEME I	Trimethylene from 1,3-Dibromopropane	3
SCHEME II	Two Mechanisms for Cyclopropane Isomerization	3
SCHEME III	Isomerization of 1,2-Dideuteriocyclopropane	4
SCHEME IV	Internal Rotation in the Trimethylene Diradical	6
SCHEME V	Possible Mechanism for Cyclopentane Formation from the Photolysis of Cyclobutanone with Ethylene	7
SCHEME VI	Isomerization of Methylcyclopropane	9
SCHEME VII	Proposed 1,4-Hydrogen Migration in the Triplet Diradical Produced from Methylene Addition to 2-Butene	24
SCHEME VIII	Alternate Mechanism for 3-Methyl-1-Butene Formation in the Reaction of Triplet Methylene with 2-Butene	25

	<u>Page</u>
SCHEME IX Bell's Proposal for the Triplet 1,3-Diradical	28
SCHEME X Reaction of Dideuteriomethylene with Ethylene	29
SCHEME XI Pyrazoline Decomposition	30
SCHEME XII Cleavage Reaction in 4,4-Dimethyl-1-Pyrazoline Thermolysis	32
SCHEME XIII Structure of 2-Methyl-1-Butene- <u>d</u> ₂ from 3,4- Dimethyl-5,5-dideuterio-1-pyrazoline	32
SCHEME XIV Configuration of the Intermediate from <u>cis</u> -3,4- Dimethyl-1-pyrazoline	33
SCHEME XV Configuration of the Intermediate from <u>trans</u> - 3,4-Dimethyl-1-pyrazoline	34
SCHEME XVI Tetrahydrofuran Photolysis	39
SCHEME XVII Trimethylene from Cyclobutanone	40
SCHEME XVIII 1-Pyrazoline Photolysis	60
SCHEME XIX Photosensitization Mechanism	70
SCHEME XX Butenes from Methyl Substituted Trimethylene Intermediate	71
SCHEME XXI Proposed Equilibration of the Intermediates from <u>cis</u> - and <u>trans</u> -3,5-Dimethyl-1-pyrazoline	76
SCHEME XXII 1,4-Hydrogen Migration in Diradical Produced from 3,5-Dimethyl-1-pyrazoline	77
SCHEME XXIII Possible Routes for Cleavage Reactions	80
SCHEME XXIV Cleavage Mechanism in 3-Methyl-1-Pyrazoline Photolysis	81

PART II

TABLE OF CONTENTS

	<u>Page</u>	
LIST OF TABLES	xiv	
LIST OF FIGURES AND SCHEMES	xv	
<u>CHAPTER I</u>	<u>Introduction</u>	
	The Tetramethylene Diradical (Cyclobutane Thermolysis)	109
	Tetrahydropyridazines	116
<u>CHAPTER II</u>	<u>Proposal</u>	125
<u>CHAPTER III</u>	<u>Results and Discussion</u>	
	(A) Attempted Synthesis of 3,4,5,6- Tetrahydropyridazine	126
	(B) Kinetics	128
	SUMMARY	135
<u>CHAPTER IV</u>	<u>Experimental</u>	136
	Attempted Synthesis of 3,4,5,6- Tetrahydropyridazine	136
	Kinetics	139

LIST OF TABLES

	<u>Page</u>
TABLE 1 Base Catalyzed 3-Methylcyclohexene Tautomerization	122
TABLE 2 Azo Compound Tautomerization	130

LIST OF FIGURES

		<u>Page</u>
FIGURE 1	Proposed Energy Profile Diagram for Cyclobutane Thermolysis	113
FIGURE 2	Diradical in 3,6-Diphenyl-3,4,5,6-Tetrahydropyridazine Decomposition	123
FIGURE 3	Nmr Spectra of Hexahydropyridazine and a Mixture of 3,4,5,6-Tetrahydropyridazine plus 1,4,5,6-Tetrahydropyridazine	127
FIGURE 4	Rate Plot for 3,4,5,6-Tetrahydropyridazine Tautomerization	132
FIGURE 5	Rate Plot for Azoethane Tautomerization	133
FIGURE 6	Rate Plot for 1-Pyrazoline Tautomerization	133

LIST OF SCHEMES

SCHEME I	Proposed Mechanism for Cyclobutane Thermolysis	110
SCHEME II	Reaction Scheme for <u>cis</u> - and <u>trans</u> -1,2-Dimethylcyclobutane Thermolysis	111
SCHEME III	Frey's Proposal for Dimethylcyclobutane Thermolysis	112
SCHEME IV	Mechanism for Hexene and Cyclohexane Formation in the Photolysis of Cyclobutanone with Ethylene	115
SCHEME V	Mechanism for Cyclobutanone Photolysis	115
SCHEME VI	Tautomerization of 3,4,5,6-Tetrahydropyridazines	117

PageSCHEME VII Cyclobutanes from 1,4,5,6-Tetrahydropyridazines 119

SCHEME VIII Decomposition of 2-Pyrazolines to give Cyclo-
propanes and Olefins 119

SCHEME IX Probable Intermediate in Azo Tautomerization 120

SCHEME X Tautomerization of Methylenecycloalkanes 120

SCHEME XI Tautomerization of 2-Methyl-1-pentene 121

SCHEME XII Decomposition of 3,6-Diphenyl-3,4,5,6-Tetra-
hydropyridazine 123

SCHEME XIII Probable Reaction Mechanism for the Base
Catalyzed Tautomerization of 3,4,5,6-Tetra-
hydropyridazine

CHAPTER I

HISTORICAL

Introduction

Much controversy has surrounded the trimethylene diradical since it was first proposed, in 1935, as a possible intermediate in the thermal isomerization of cyclopropane^{1a}. Since then, the thermolysis of cyclopropane and various substituted cyclopropanes has been studied in great detail by many workers, but the existence of a trimethylene diradical was never proven or disproven by these reactions.

In the early 1950's, the addition of methylene to olefins became another possible source of trimethylene diradicals. Most workers feel that singlet methylene does not give rise to a trimethylene diradical on adding to olefins, while triplet methylene does.

The thermolysis of 1-pyrazolines has been proposed to proceed through a trimethylene diradical and has been studied in detail by various workers. Very little work has been done on the photolysis of these compounds, and the present study attempts to remedy this situation by photolyzing various 1-pyrazolines. This would presumably produce trimethylene diradicals of higher energy content than those produced from thermolysis reactions.

The photolysis of cyclobutanone has also been proposed to produce trimethylene diradicals by some, but most workers do not favor this.

Finally, a theoretical treatment of trimethylene diradicals has recently been carried out by Hoffmann, in which an attempt is made to predict the behavior of these intermediates produced in various electronic states. This study will also attempt to correlate Hoffmann's predictions with the properties of photochemically produced trimethylene diradicals.

(a) Trimethylene as an Intermediate in Cyclopropane Thermolysis

The trimethylene diradical was first suggested by Chambers and Kistiakowsky^{1a}, as a possible intermediate in the thermal isomerization of cyclopropane to propylene. They found that the reaction was homogeneous, unimolecular, and that the high pressure rate constant (k_{∞}) was described by the equation:

$$\log k_{\infty} = 15.17 - 65,000/2.3RT$$

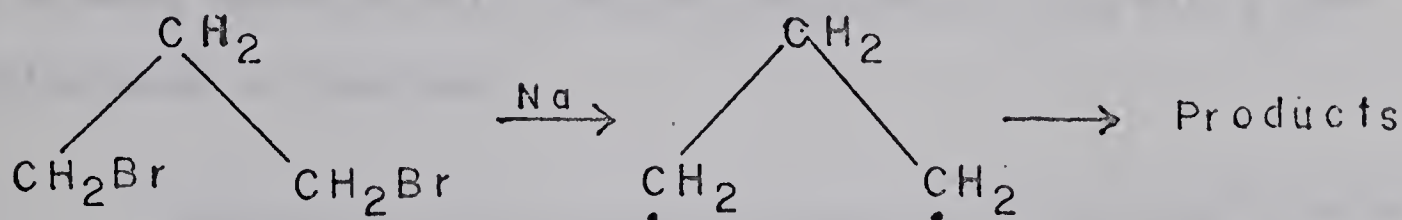
The authors concluded that the isomerization could proceed through a ring opening mechanism to give a trimethylene diradical or by a concerted hydrogen transfer mechanism. They did not favor one mechanism over the other because of insufficient data.

In 1938, Bawn and Hunter² treated 1,3-dibromopropane vapor with sodium vapor in the presence of varying amounts of inert gas (N_2). They obtained a mixture of cyclopropane and propylene as the products, with the propylene yield varying from 36.5% at 1.69 mm of nitrogen to 12.8% at 2.95 mm of nitrogen.

They assumed that propylene formation was a heterogeneous reaction taking place at the walls of the reaction vessel. The authors

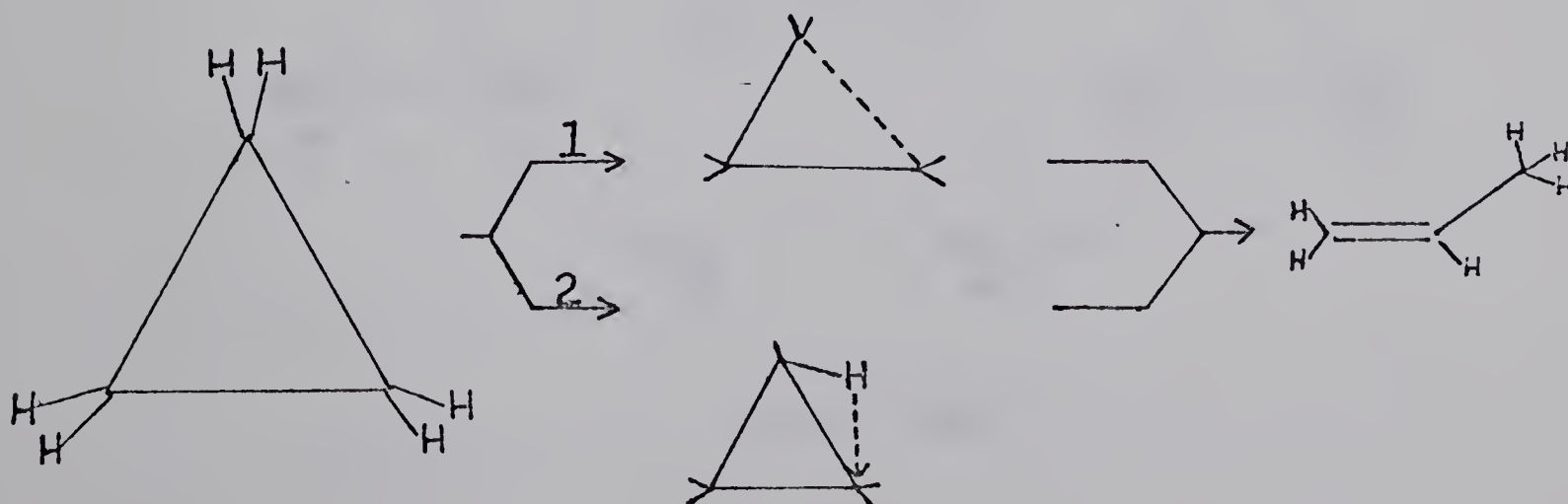
postulated the formation of the trimethylene diradical as an intermediate in the reaction.

SCHEME I



Corner and Pease^{1b}, in 1945, also came to the conclusion that the mechanism for cyclopropane isomerization to propylene involved the trimethylene diradical as an intermediate. However, Pritchard, Sowden and Trotman-Dickenson^{1c}, rejected the mechanism of Corner and Pease on the basis that their own data agreed with the theory developed by Slater^{1d}, which predicted the rate of isomerization of cyclopropane using hydrogen transfer as the critical reaction coordinate (Scheme II, Path 2), and not carbon-carbon cleavage (Path 1).

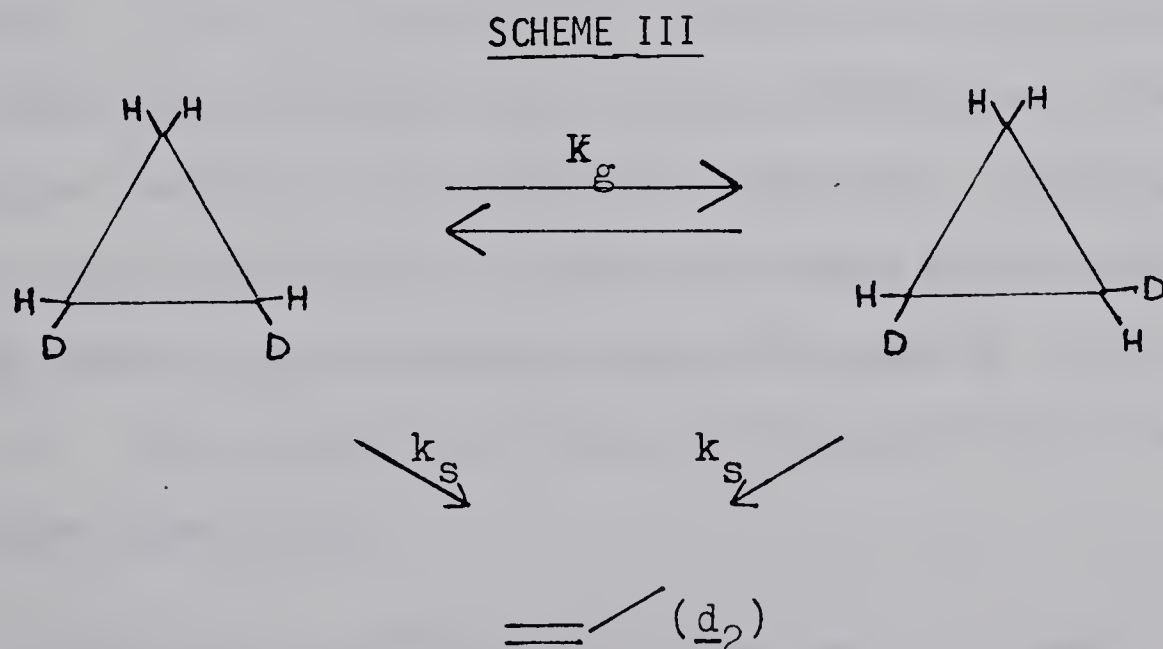
SCHEME II



Slater's theory implies that a free flow of energy between the various vibrational modes of cyclopropane is forbidden. However, Butler and Kistiakowsky^{3a,b} showed that a free flow of energy is probable when they obtained approximately the same yields of various olefin products on allowing photochemically produced methylene to react with either cyclopropane or propylene.

Subsequent workers, namely Lindquist and Rollefson^{1e}, McNesby and Gordon^{1f}, have also supported the Slater model. The former group isomerized cyclopropane-t₁ and studied the isotope effect. The latter group ruled out a radical chain mechanism and "probably any other radical mechanism" on the basis that they failed to observe any appreciable amount of deuterium in the products when they isomerized cyclopropane in the presence of deuterium.

In 1958, Rabinovitch et al.^{1g} heated both cis- and trans-1,2-dideuteriocyclopropane and found reversible geometrical isomerization (Scheme III).



From their data they found that $k_g > k_s$.

$$k_g = 10^{16.0} e^{-64,200/RT} \quad (\text{geometrical isomerization})$$

$$k_s = 10^{15.2} e^{-65,500/RT} \quad (\text{structural isomerization})$$

$$\text{Average } k_g/k_s = 12 \quad (444^\circ \text{C})$$

They concluded that the trimethylene diradical is the intermediate for geometrical isomerization, but did not conclude anything about the role of a trimethylene diradical in the formation of propylene.

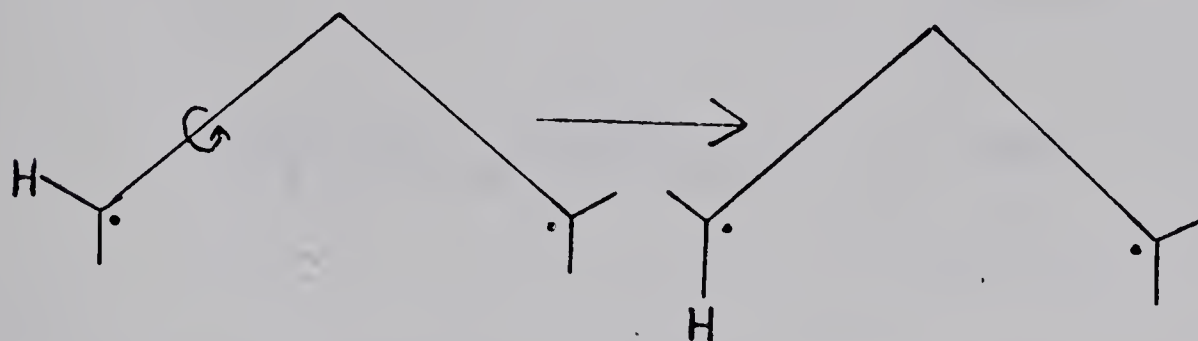
Rabinovitch et al.⁴ followed this further by studying the addition of methylene to trans-ethylene-d₂, and found the average value of $k_g/k_s = 14.2$ when 3100 Å light was used to produce methylene from ketene. When 3600 Å light was used $k_g/k_s = 18.7$. Because the k_g/k_s ratios are so similar, the authors concluded that the transition state for both processes should be similar.

On analyzing the data from the thermal isomerization of cyclopropane-d₂ further, Schlag and Rabinovitch^{1h} found that the Slater theory can account for the results if the cyclopropane-d₂ has 13 or 14 vibrational modes active. This is the same number of active modes required by the Slater theory for cyclopropane isomerization (cyclopropane actually has 21 vibrational modes but 7 are considered degenerate). However, the presence of two deuterium atoms in the cyclopropane should remove the degeneracy found in cyclopropane and raise the number of active vibrational modes to 21. This results in a further criticism of Slater's theory for cyclopropane isomerization.

Benson and DeMore⁵ have calculated that ring closure of the

trimethylene diradical at 25° should be roughly ten times faster than propylene formation and also that rotation (Scheme IV) about a carbon-carbon bond in trimethylene is faster than propylene formation.

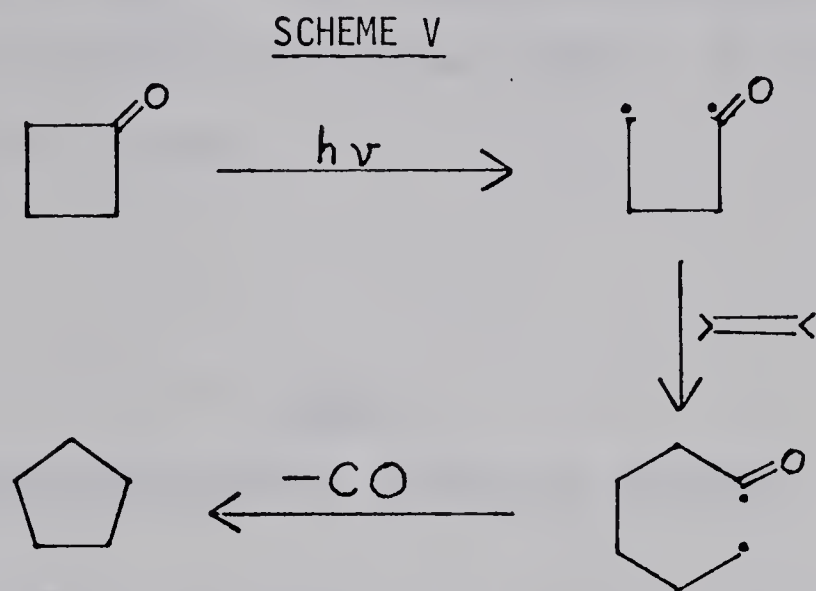
SCHEME IV



This would account for the faster rate of geometrical isomerization in cyclopropane- d_2 than structural isomerization. Benson^{6a} has also calculated that the life-time of the trimethylene diradical at 444 C is in the order of $10^{-10.5}$ seconds, which is much faster than the collision frequency at 1 atmosphere pressure. This could explain the failure of trimethylene* from cyclopropane isomerization to be trapped by oxygen^{1h}, nitric oxide^{6b} or ethylene⁷. Flowers and Frey⁷ reported the trapping of trimethylene diradical from cyclobutanone photolysis by using ethylene as the trapping agent. However, Klemm et al.⁸ could not reproduce this result when they repeated Flowers and Frey's experiment.

*Benson's calculations are based on the trimethylene diradical being a true diradical (pair of spectroscopic doublets). This should not be confused with Hoffmann's trimethylene intermediate to be discussed later (Page 40).

Flowers and Frey did not, however, consider alternative possibilities to the production of cyclopentane such as:



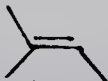
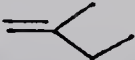


The thermal isomerization of cyclopropane and cyclopropane- \underline{d}_6 was reported by Blades¹ⁱ, in 1961. He found that k_H/k_D varied with pressure having a value of 1.89 at lower pressures and increasing to 2.18 at higher pressures. These corresponded to the values calculated for a primary isotope effect in cyclopropane, so the author concluded that a trimethylene diradical was impossible (carbon-carbon bond cleavage) and that the rate determining step must involve carbon-hydrogen (or C-D) bond cleavage. However, Rabinovitch et al.^{1j} considered Blades' results and argued that k_H/k_D should decline as pressure decreases because the present formulation of cyclopropane- \underline{d}_6 is characterized by a classical³⁹ empirical Kassel \underline{s} value greater than for cyclopropane, and thus by a slower falloff, since \underline{s} rises toward the total number of active modes as the classical treatment becomes more valid. They conclude that this case involves a combined primary-secondary isotope effect. Benson and Nangia⁹ criticize Blades' conclusion and argue that Blades is in error rejecting the diradical mechanism, and in fact, they use Blades' data to

support the diradical mechanism.

Flowers and Frey^{6b,10} have reported the thermal isomerization of cis- and trans-1,2-dimethylcyclopropane (DMCP). The results obtained for 430.9°C. are given in Table 1.

TABLE 1
DIMETHYLCYCLOPROPANE THERMOLYSIS PRODUCTS

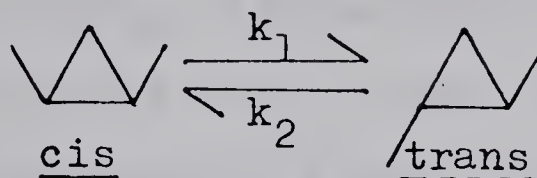
Dimethyl- cyclopropane	$10^6 k_s^a, \text{sec.}^{-1}$			
				
<u>cis</u> -	9.42	7.61	5.45	5.15
<u>trans</u> -	5.40	3.33	5.45	5.15
$E_a, \text{kcal./mole}(\log_{10} A)$				
<u>cis</u> -	61.2 (13.96)	61.4 (13.92)	62.3 (14.08)	61.9 (13.93)
<u>trans</u> -	62.9 (14.30)	63.6 (14.40)	62.3 (14.08)	61.9 (13.93)

^a k_s : structural isomerization rate constant

They also found that for cis to trans isomerization at 430.9 C,
 $k_g = 6.56 \times 10^{-4} \text{ sec.}^{-1}$, and $k_g = 10^{15.25} e^{-59,420/RT}$.

In this case, then, we have $k_g/k_s = 100$, which is approximately 8.5 times

larger than the k_g/k_s ratio in the case of 1,2-dideuteriocyclopropane¹⁹.
The authors also found that for



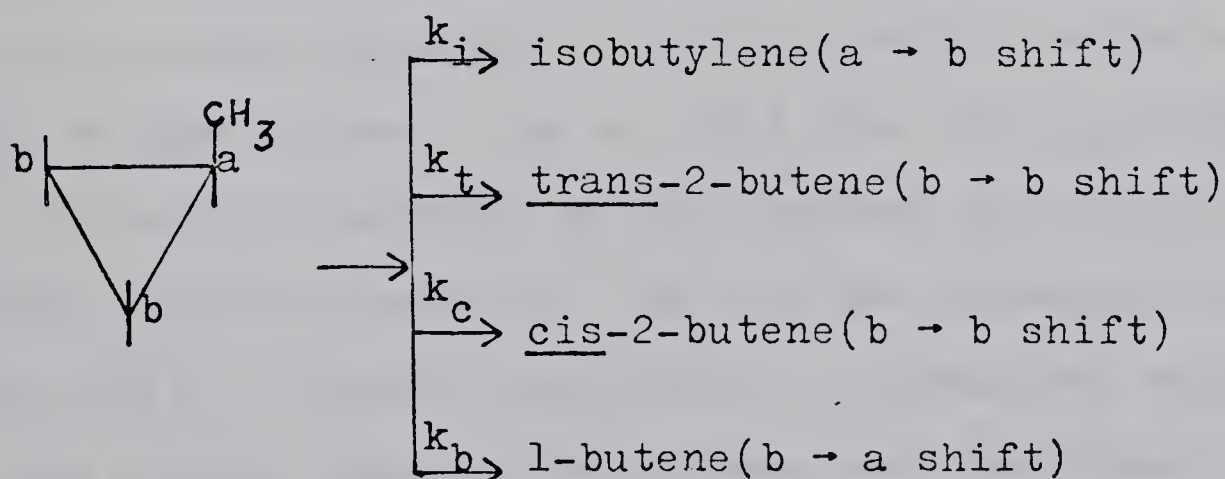
at 430.9°C.

$$k_2/k_1 = K' = 0.425$$

It was suggested by the authors that their experimental results favor an expanded ring mechanism for olefin formation, rather than a hydrogen migration mechanism, but were careful not to suggest the formation of a diradical as an intermediate.

The thermal isomerization of methylcyclopropane has also been studied^{11,12}.

SCHEME VI



Setser and Rabinovitch¹² found that at the center of the temperature range used (~400°C.) that,

$$k_t:k_i:k_c:k_b = 0.301:0.178:0.717:1.00$$

Chesick¹¹, for the same reaction, found that,

$$k_t:k_i:k_c:k_b = 0.304:0.149:0.645:1.00$$

at 447°C. This gives $(k_t+k_c)/k_b = 0.95$ for Chesick's work, and $k_t+k_c/k_b = 1.02$ for Setser and Rabinovitch's work. Setser and Rabinovitch came to the conclusion that a combination of 1 and 2 (Scheme II) must be included in the mechanism for the thermal isomerization of methylcyclopropane.



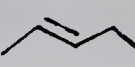

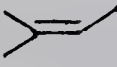
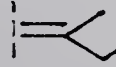
(b) Trimethylene as an Intermediate in the Addition of Methylene to Olefins

A second method of producing 'hot' cyclopropanes which isomerize, is by the addition of methylene (either thermally or photochemically produced) to olefins. In 1950, Kistiakowsky and Rosenberg^{13a} reported the reaction of ketene with ethylene and propylene. From kinetic data, the authors proposed the initial formation of trimethylene diradical, which then went on to form the products.

I Singlet Methylene.- Skell and Woodworth^{13b} reported in 1956, that when methylene produced photochemically from diazomethane reacted with either cis- or trans-2-butene in gas or liquid phase, the only products were the 1,2-dimethylcyclopropanes and the 2-pentenenes with the cis and trans geometry completely preserved. They used this stereospecificity to conclude that a 1,3-diradical could not be an intermediate, because if it were, then rotations about the carbon-carbon bonds (See Scheme IV) would produce some trans products from cis starting material and vice versa. Skell and Garner^{13c} also ruled out a diradical intermediate on the basis that the rate of addition of dibromomethylene to various olefins showed no correlation whatsoever with the rate of addition of trichloromethyl, which is assumed to add to a double bond from one end. In 1959, Skell and Woodworth^{13a} reported the product distribution for the photolysis

of diazomethane in the presence of cis- and trans-2-butene (Table 2).

TABLE 2
PRODUCTS FROM METHYLENE ADDITION TO 2-BUTENE^{13d}

2-Butene Isomer	Phase	Product %					
							
<u>cis</u>	Gas (760 mm.)	44.6	1	44.6	0	9.7	0
<u>cis</u>	Liquid	47.3	trace	47.3	0	4.4	0.9 ₅
<u>trans</u>	Gas (760 mm.)	0	50.0	0	50.0	trace	0
<u>trans</u>	Liquid	0	63.0	0	36.1	0.9	0

They observe that the 2-methyl-2-butene may be produced from C-H insertion of the methylene, or alternately, the dimethylcyclopropane initially formed may have enough excess energy to isomerize. However, if the latter is true, one should also see some trans-2-pentene from the reaction with cis-2-butene and cis-2-pentene from the reaction with trans-2-butene. The analysis in this work was all carried out using i.r. spectra and is not as accurate as later work in which the analyses were performed using gas chromatography.

The photochemical decomposition of ketene at 3130 Å in the presence of ethylene was studied in some detail by Frey and Kistiakowsky^{13e}, and they found that in a 1:7.5 mixture of ketene to ethylene, the ratio

of cyclopropane to total C_3 product tended asymptotically to value of 0.62 with increasing pressure. With a 1:7.5:143 mixture of ketene, ethylene and carbon dioxide, the value tended to approximately 0.8. The authors did a rough calculation to obtain the excess* energy content of the cyclopropane initially formed, and found a value of 97 kcal./mole.

Rabinovitch et al.⁴ allowed methylene to react with trans-ethylene- d_2 , and found the high pressure (2800 cm) limiting yield of cyclopropane in the C_3 products was about eighty-five percent. It was also found that the yield of cis-cyclopropane- d_2 decreased from 48% to 17% on going from 10 cm to 2800 cm pressure. The above eighty-five percent figure for the limiting yield of cyclopropane agrees quite well with that calculated by DeMore and Benson⁵ who, by using simple Rice-Ramsperger-Kassel theory predicted that ring closure of the trimethylene diradical should be about ten times faster than hydrogen migration. Therefore, the limiting yield of cyclopropane should be near ninety percent.






Later, and presumably more accurate, estimations of the excess energy content of the initial cyclopropane formed in the reaction of methylene with ethylene were obtained by Setser and Rabinovitch^{13f}. They found that for both the photochemical (4358 \AA) and thermal decomposition of diazomethane, the initially formed cyclopropane had approximately 111 kcal./mole excess energy. For the photolysis of ketene (3200 \AA) the cyclopropane initially formed had an excess energy of approximately 104 kcal./mole. In these calculations, the authors assume that methylene

*Excess energy is defined as the total energy possessed by the molecule above its heat of formation (ΔH_f^0).

reacts with a double bond in a three-centered mechanism to form a 'hot' cyclopropane immediately, and that all propylene, except that which is formed by insertion, arises from subsequent ring opening of the 'hot' cyclopropane. DeMore and Benson⁵, however, "believe that the detailed mechanism must include formation of a short lived diradical as the initial step for both singlet and triplet methylene." Moreover, DeMore and Benson's calculations, based on a diradical model, predict the following high pressure limiting yields of products for the addition of methylene to trans-ethylene-d₂; trans-cyclopropane-d₂, 77.5%; cis-cyclopropane-d₂, 12.5%; and propylene-d₂, 10%. The results actually found by Rabinovitch et al.⁴, at 2800 cm. pressure are trans-cyclopropane-d₂, 68%; cis-cyclopropane-d₂, 17%; and propylene-d₂, 15%. This is extremely good agreement considering the nature of DeMore and Benson's calculations, the fact that 2800 cm. pressure may not be sufficient to completely quench the isomerization of all the cyclopropane, and that some propylene may be formed by direct insertion into a C-H bond.

The reaction of methylene with propylene and cyclopropane has been studied by Butler and Kistiakowsky^{3a,b}, as mentioned previously. Their results for ketene photolysis at 3100 Å are given in Table 3.

TABLE 3
PRODUCTS FROM METHYLENE ADDITION
TO CYCLOPROPANE AND PROPYLENE

Substrate	P _{total} mm.	Product %				
						
Cyclopropane ^a	440	77	11.5	5.8	3.3	2.5
Cyclopropane ^a	65.8	27.9	28.8	19.4	14.7	9.1
Propylene ^b	1970	71	17.8	4.0	3.7	3.5
Propylene ^c	101	53.5	25.5	8.4	6.7	5.9

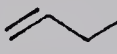



^aAverage of 2 runs; ^baverage of 3 runs; ^caverage of 5 runs.

For the methylene-cyclopropane reaction the authors found that a plot of B vs. the reciprocal of pressure extrapolated to zero, where B equals total butenes/methylcyclopropane. This is to be expected, since the higher the pressure, the greater the amount of 'hot' methylcyclopropane which is deactivated by collision before it has a chance to isomerize to olefin. Also, the decrease in butene yield, with increasing pressure in the case of methylene plus propylene, is to be expected regardless of which mechanism one invokes (a diradical mechanism or a concerted three-center type). The authors also state that the high pressure yields of butenes for methylene plus propylene may be interpreted in terms of relative rates of attack of methylene on various types of bonds. However,

this statement precludes the possibility of a diradical which when completely 'cooled' by collisions may still partition itself between closing to methylcyclopropane and rearranging to form butenes. Unfortunately, the data does not permit a distinction between the two mechanisms because of the presence of direct insertion reactions.

The relative ratios of butene yields from the methylene reactions to those of the thermal isomerization of methylcyclopropane are shown in Table 4.

TABLE 4
RELATIVE BUTENE YIELDS FROM VARIOUS
'HOT' METHYLCYCLOPROPANES

Source	Pressure mm.				
$\text{CH}_2 + \Delta$	65.8	1.00	0.67	0.51	0.32
$\text{CH}_2 + \Delta$	440	1.00	0.505	0.287	0.217
$\text{CH}_2 + \text{C}_3\text{H}_6$	101	1.00	0.330	0.263	0.232
$\text{CH}_2 + \text{C}_3\text{H}_6$	1970	1.00	0.235	0.213	0.197
Thermal Δ^a	-	1.00	0.717	0.301	0.178
Thermal Δ^b	-	1.00	0.645	0.304	0.149

^adata of Setser and Rabinovitch¹²; ^bdata of Chesick¹¹







We see that the order is the same in every case and indeed, the actual values are quite similar when methylene plus cyclopropane is compared with the thermal data for methylcyclopropane. The data for methylene plus propylene is much more out of line, which is to be expected because of the presence of insertion reactions. However, the ratios are in the same order as the others. Again, this data does not enable one to prove or disprove the presence of a diradical as an intermediate.

A later study of the reaction of methylene with propylene by Dorer and Rabinovitch^{13j} fairly well confirmed the results of Butler and Kistiakowsky. They found that at high pressures the yield of methylcyclopropane levelled out at 75%; 1-butene at 15-16% and other C₄ olefins at 3-5%. However, in the presence of added oxygen, which would presumably quench any free radical or triplet reaction, they found that methylcyclopropane decreased to 64%; 1-butene increased to approximately 20% and other C₄ olefins increased to 5-7%.

Probably the most extensively studied of the reactions of methylene with olefins has been the addition of methylene to cis- and trans-2-butene. This was first reported in some detail by Skell and Woodworth^{13b,d}, but later work by others seems to be more detailed, with more accurate analyses. In 1959, Frey^{13g} reported the reaction of diazomethane photolyzed at 4358 Å in the presence of cis- and trans-2-butene at room temperature. His results are given in Table 5.

TABLE 5

PRODUCTS FROM METHYLENE ADDITION TO 2-BUTENE^{13g}

Substrate	P _{total} ^{mm.}	C ₅ /total C ₅ (X100)					
							
<u>t</u> -Butene-2	<10	15-20	~5	40	7	20	8
<u>t</u> -Butene-2	>300	42	2-3	43	1	12	<2
<u>c</u> -Butene-2	<10	13 ^a	10 ^a		32 ^a		
<u>c</u> -Butene-2	>400	<10 ^a	33 ^a		40 ^a		
<u>t</u> -Butene-2 ^b	Liq. (-70°C.)	51		39.7		9.2	
<u>t</u> -Butene-2 ^b	1200	"Similar to liquid"					

^a Only ones reported; ^b Earlier study by Frey^{13h} using 3100 Å radiation.







All the products reported levelled out to a fairly constant value at high pressures. The author claims that the upper pressure was not reached in the case of trans-2-butene because there was always some of the non-stereospecific (cis) cyclopropane present. This again, however, precludes the possibility of a 1,3-diradical being formed. A better test for the upper pressure limit would be the presence of cis-2-pentene which can only arise from either the isomerization of 1,2-dimethylcyclopropane or from the geometrical isomerization of trans-2-pentene. At the upper pressure limit both these processes should be quenched and no cis-2-pentene seen at all. When we compare these results with those of Skell and

Woodworth^{13d}, we see that they are similar in some respects, namely, the increase in stereospecificity and decrease in 2-methyl-2-butene yield with increasing pressure. However, in the case of trans-2-butene, Skell and Woodworth report a trace and 0.9 percent for the yield of 2-methyl-2-butene in gas (760 mm.) and liquid phases respectively. Frey reports 12% (>300 mm.) and 9.2 respectively. This is a large discrepancy, which is obviously indicative of the fact that the analysis in one or maybe both cases is not correct.

Doering and LaFlamme¹³ⁱ had earlier reported trans-1,2-dimethylcyclopropane, 27%; trans-2-pentene, 59%; and 2-methyl-2-butene, 14%, for the photolysis (3100 Å) of diazomethane in liquid trans-2-butene at -75 C. For cis-2-butene at -75 C, they reported 99% cis-1,2-dimethylcyclopropane and less than 1% other C₅ products. These results are not even close (except for the yield of 2-methyl-2-butene) to those of Frey.

Setser and Rabinovitch^{13f} allowed methylene, thermally produced from diazomethane, to react with cis-2-butene. Their results along with Bader and Generosa's^{13k} photochemical results are shown in Table 6.

TABLE 6
PRODUCTS FROM METHYLENE ADDITION
TO CIS-2-BUTENE^{13f}

Pressure mm.	Temp. °C.	C ₅ /total C ₅ , %					
							
~10	250	16-18	20	6-7	~40	~18	2-3
~40	250	14-16	~30	3-4	~40	~16	~1
1000	250	~5	~45	~1	~35-38	~15	0
<10 ^a	25(hν)	~18	12	22	30	19	

^a Bader and Generosa.







These results agree fairly well with each other if one considers that the initial products in the work of Bader and Generosa are probably 'hotter' and are not getting quenched as fast because of the lower pressure. They also agree quite well with previously reported work^{13g,14}. In all of the foregoing, it has been assumed or implied by the authors that methylene (singlet) reacts initially with the double bonds of olefins in a three-center mechanism to form a 'hot' cyclopropane which will then isomerize to various olefins unless quenched very rapidly. For the most part the lone dissenting voice to this mechanism has been Benson^{5,6a,9}, who has succeeded in explaining almost all the presently known results using a very short lived 1,3-diradical as the initially formed species.

II Triplet Methylene.- Contrary to the foregoing dissention concerning singlet methylene, the addition of triplet methylene to double bonds is almost invariably believed to proceed via the initial formation of a trimethylene 1,3-diradical.

The work of Herzberg^{15a,b,c} has been interpreted to mean that the ground state of methylene is a triplet. When methylene is produced in the presence of high concentrations of inert gas, the resulting reacting species is believed to be triplet methylene, which was initially formed in the singlet state but, through collisions with the inert gas, is degraded to the triplet ground state before reacting with any hydrocarbon present. Most of the work with triplet methylene has taken place since Herzberg's findings, but undoubtedly, some of the earlier results were due to fairly large concentrations of triplet methylene, or example the work of Frey and Kistiakowsky^{13e}, when they added methylene to ethylene in the presence of a large excess of carbon dioxide.

Some of the earliest work designed primarily for the study of triplet methylene was that of Frey¹⁶. Working in the total pressure range of 2100-3200 mm. with argon as the inert gas and with a cis-2-butene to diazomethane ratio greater than 4:1, he reported the results shown in Table 7.

TABLE 7
PRODUCTS FROM TRIPLET METHYLENE ADDITION
TO CIS-2-BUTENE

Ratio of Argon to <u>cis</u> -2-Butene	Product %					
						
7.6	9.5	44.3	2.4	30.4	1.9	12.9
134	18.0	33.3	8.8	24.9	6.6	8.4
356 ^a	3.6	50.9	0.9	27.7	1.8	15.0
850	24.0	28.4	12.7	19.1	9.2	6.6
1600	27.1	28.1	16.5	17.0	10.5	4.0

^a4 mm. O₂ added.

The author concludes from this data, that 2-methyl-2-butene and 2-methyl-1-butene are not products of triplet methylene addition, whereas 3-methyl-1-butene is a product. One immediately sees that on going to high concentrations of argon that stereospecificity is lost in the cyclopropane products. Earlier work by Anet et al.¹⁴ showed the same loss of stereospecificity, but was criticized by Frey on the grounds that the inert gas (N₂) pressures used were too low (~600 mm.) to ensure quenching of the geometrical isomerization of the 'energized' cis-dimethylcyclopropane, since nitrogen is not as efficient as cis-2-butene in removing excess energy by collision. DeMore and Benson⁵ have in turn questioned the work

of Frey on much the same grounds that Frey criticized Anet et al. That is, by replacing cis-2-butene by argon or nitrogen leads to decreased deactivation of efficiency. This is supported to some extent by the work of Simons et al.¹⁷ who by using a 'stepladder' model for collisional deactivation estimated that N₂ removed around six kcal. per collision, while ethylene removed six to ten kcal. and possibly as much as thirty. Butene would certainly be expected to be much more efficient than ethylene for collisionally removing excess energy.

In 1965, Bader and Generosa^{13k} reported favorable evidence for the existence of triplet methylene. They allowed methylene (produced by the photolysis of diazomethane) to react with cis-2-butene in the presence of varying pressures of inert gas (nitrogen, carbon tetrafluoride, xenon and helium). At high pressures (800 mm) of carbon tetrafluoride they found the following product distribution:

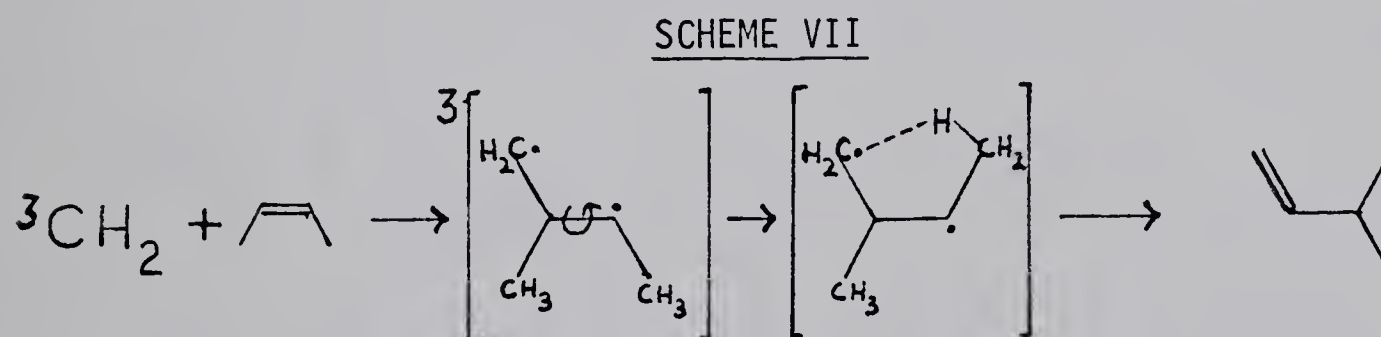
TABLE 8

PRODUCTS FROM TRIPLET METHYLENE ADDITION
TO CIS-2-BUTENE^{13k}

<u>trans</u> -DMCP	20%
<u>cis</u> -DMCP	20%
<u>cis</u> -2-Pentene	15%
<u>trans</u> -2-Pentene	17%
2-Methyl-2-butene	4%
3-Methyl-1-butene	24%

Their low pressure results have already been given in Table 6. These results are in very close agreement with Frey's, when one considers the fact that carbon tetrafluoride is probably quite a bit more efficient than nitrogen at causing singlet to triplet conversion of methylene because of its greater number of vibrational degrees of freedom. Bader and Generosa found that the yield of trans-dimethylcyclopropane (trans-DMCP) first decreased and then increased with increasing pressure, when nitrogen or carbon tetrafluoride was used. However, when just cis-2-butene or nitrogen with ten percent oxygen added was used, the yield of trans-DMCP tended to near zero with increasing pressure. Clearly, the initial decrease of trans-DMCP in the case of carbon tetrafluoride and nitrogen is due to increased collisional deactivation of the initially formed 'hot' cis-DMCP. However, as the pressure increases further, a new source of trans-DMCP arises and the authors ascribe this to the increasing concentration of triplet methylene. Conversely, the yield of cis-DMCP goes through a maximum (reaction of cis-2-butene with triplet methylene) and then falls off with increasing pressure. The yield of cis-2-pentene decreases from around thirty percent to around fifteen percent over the pressure range studied and the yield of trans-2-pentene goes through a minimum, then increases and levels off at about seventeen percent. The yield of 2-methyl-2-butene decreases towards zero with increasing pressure. In the experiments with carbon tetrafluoride and xenon at pressures below 25 mm., the yield of 3-methyl-1-butene is very high (~30%), then drops very rapidly with increasing inert gas pressure and then above 25 mm. rises continuously to a value of about twenty-four percent. The effect was not observed with nitrogen, whose lowest pressure

used was 14 mm. Setser and Rabinovitch^{13f} noticed the same effect in their studies on the pyrolysis of diazomethane, in the presence of cis-2-butene. The authors conclude that there may be another mode of formation for 3-methyl-1-butene, which has an inverse pressure dependence and operates only at very low pressures, but not compellingly so, because there was very large scatter in their results at low pressures. The authors point out that Flowers and Frey¹⁰ found only trace amounts of 3-methyl-1-butene even at pressures as low as 6.5 mm., when they thermally isomerized cis-DMCP. It was also found that the yield of 3-methyl-1-butene was reduced to almost zero over the whole pressure range on the addition of oxygen. So far, there has been only speculation on the reason for the very high yield at low pressure, but at the higher pressures Bader and Generosa propose the following:

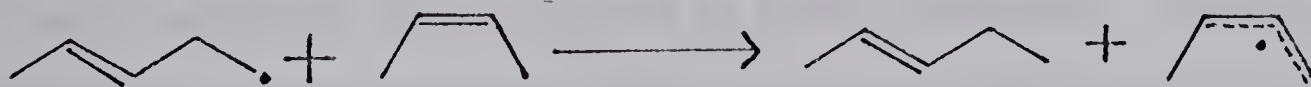
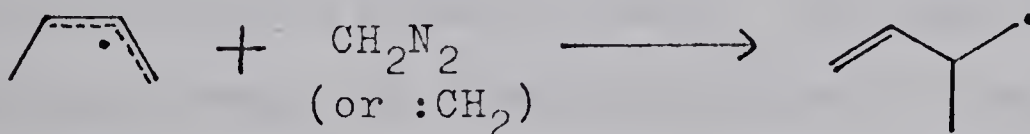
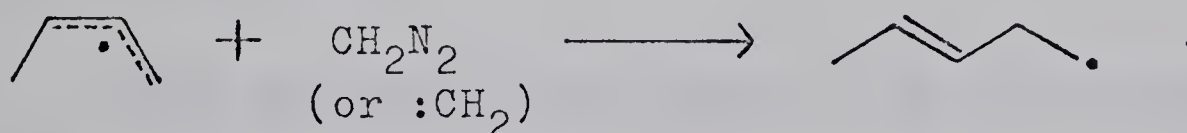


This scheme must include spin inversion to the singlet presumably before the 1,4-hydrogen shift. It is also pointed out by the above authors that DeMore and Benson suggest the 3-methyl-1-butene in all cases arises from the isomerization of a 'hot' cyclopropane structure, and that a triplet intermediate is not necessary to explain its appearance. However, Bader and Generosa's results do not substantiate this claim. The authors explain that no 2-methyl-1-butene was detected in their experiments because its yield is relatively small in the reaction of methylene with

2-butene, and very small amounts of reactants were used.

In view of the recent work reported by Ring and Rabinovitch¹⁸, stating that triplet methylene is capable of abstracting hydrogen atoms, another possibility arises for the formation of 3-methyl-1-butene and for the increase in trans-2-pentene with increasing inert gas pressure. They found that triplet methylene abstracts tertiary hydrogen atoms (in isobutene) almost as readily as it adds to double bonds. Presumably then, it could abstract allylic hydrogen atoms with ease also, to give allyl radicals which could react in two ways as in the following scheme:

SCHEME VIII



Of course, small amounts of ethane are also produced in this scheme. A considerable concentration of $A\cdot$ could be built up in these reactions because it is produced from the reaction of cis-2-butene with either triplet methylene or methyl radicals. This scheme could also account for the rise of trans-2-pentene yield with increasing pressure providing the cis-form of $A\cdot$ rapidly equilibrates with the trans-form. Allylic radicals are known to retain their steric configuration in solution, but little is known about their behavior in the gas phase. If $A\cdot$ does not equilibrate, then recombination of cis- $A\cdot$ with methylene or methyl radicals would produce a 'hot' species which may isomerize before being collisionally deactivated. If Scheme VIII is operative in the case of triplet methylene, then this would mean that the triplet 1,3-diradical supposedly formed by addition to the double bond gives rise to little, if any, olefin formation, but immediately after spin inversion closes to form cis- and trans-DMCP.

Scheme VIII may also have support in the work of Kopecky et al.^{19a,b} which consisted of decomposing diazomethane by benzophenone photosensitization in liquid cyclohexene. They found norcarane, 70%; 3-methylcyclohexene, 15%; 4-methylcyclohexene, 15%; and no 1-methylcyclohexene. The authors assumed that the products other than norcarane arose from singlet methylene being produced by direct photolysis. However, from previous data, singlet methylene appears to insert into vinylic C-H bonds almost as fast as allylic C-H bonds^{3a,13h,20}, but yet, the authors see no 1-methylcyclohexene which should be present in at least six to seven percent yield.



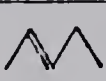

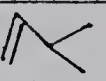
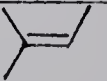

Kopecky et al. have also reported the reaction of triplet methylene (produced by benzophenone photosensitization of diazomethane) with cis- and trans-2-butene in octane solvent. For the cis-2-butene they reported two parts cis-DMCP and one part trans-DMCP only. For the trans-2-butene, they have reported trans-DMCP as the main product, a very small amount of cis-DMCP and a trace of olefin. It was concluded that spin inversion must be very rapid in solution because both butenes give nowhere near the same product ratios; hence ring closure takes place before much internal rotation can occur.

A third way of producing triplet methylene is presumably by the mercury photosensitized decomposition of ketene. Results obtained by Duncan and Cvetanovic²¹ for the reaction of methylene produced in this manner with cis- and trans-2-butene at pressures greater than 500 mm. are as follows:

TABLE 9

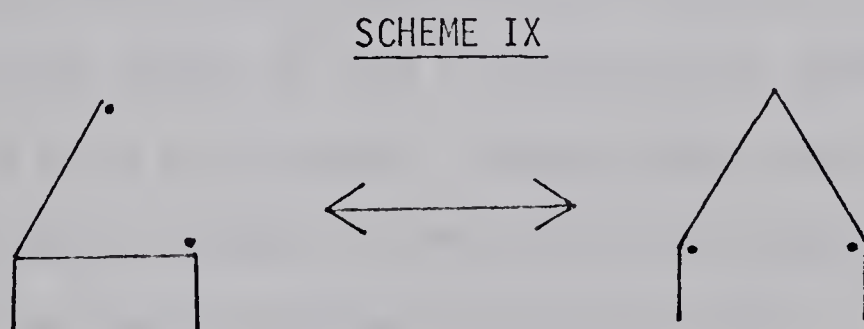
PRODUCTS FROM TRIPLET METHYLENE (MERCURY PHOTSENSITIZATION)

ADDITION TO 2-BUTENE²¹

2-Butene Isomer	Product %						
							
<u>cis</u>	31.3	24.6	12.3	19.3	8.1	3.7	0.7
<u>trans</u>	51.9	13.5	18.9	5.5	6.8	2.8	0.7

These results agree quite well with those of Frey¹⁶ and Bader and Generosa^{13k} if it is kept in mind that the initial products in this case are probably somewhat 'hotter' than those produced in previous work because the triplet energy of mercury (3P_1) atoms is around 112 kcal.mole.

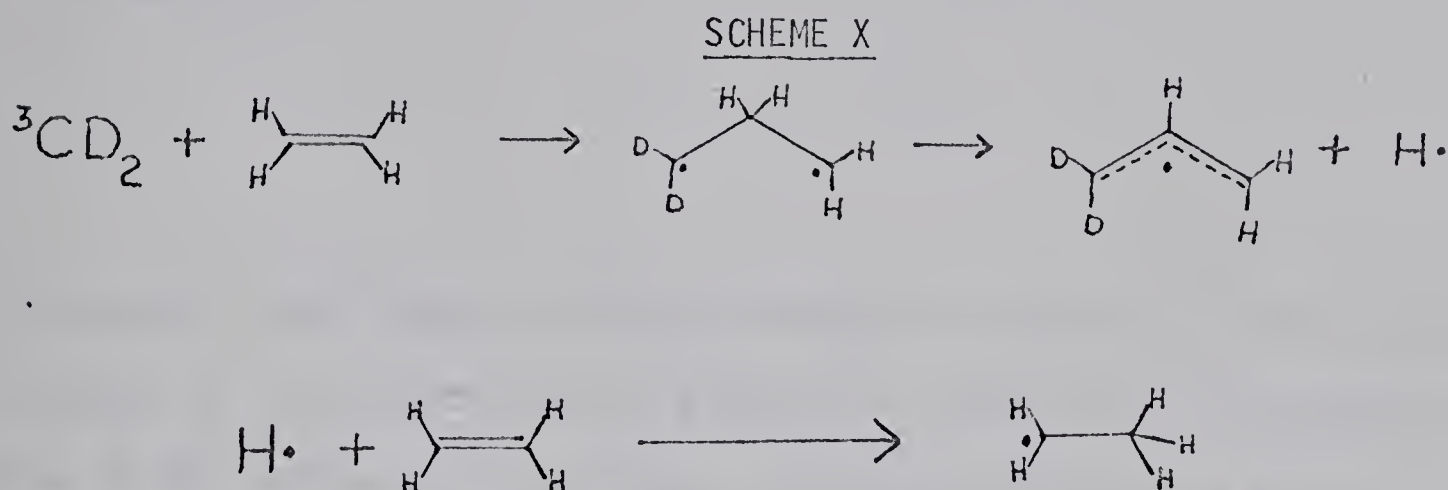
A different type intermediate for the addition of triplet methylene to olefins has been proposed by Bell^{27a,b}. He states that since linear 2-pentene is formed when triplet methylene is added to *cis*-2-butene, and since a methyl migration is not as likely as a hydrogen migration, then some other mechanism must give rise to the linear pentenes. He proposed some triplet cyclopropane species which may be thought of as a resonance hybrid of two diradicals:



Bell has also isomerized *cis*-1,2-dimethylcyclopropane using benzene and toluene as photosensitizers^{27b}. He found that the products were *trans*-DMCP, *cis*- and *trans*-2-pentene, 3-methyl-1-butene, and 1 - 3% unidentified C₅ hydrocarbons. He does not, however, give the yields of the various products. This then is used to support the above proposal (Scheme IX).

Cvetanovic et al.²⁸ have disputed Bell's proposal by applying the results obtained when triplet dideuteriomethylene was reacted with ethylene. Two minor products are formed, *n*-butane and 1-pentene. They

found that the n-butane was 99.3%- \underline{d}_0 and 0.7%- \underline{d}_1 , and the 1-pentene is 95%- \underline{d}_2 , 2% each of \underline{d}_1 and \underline{d}_3 , and 1%- \underline{d}_0 . They concluded that there are ethyl radicals- \underline{d}_0 and allyl radicals- \underline{d}_2 present, and that these may only arise from the following Scheme:



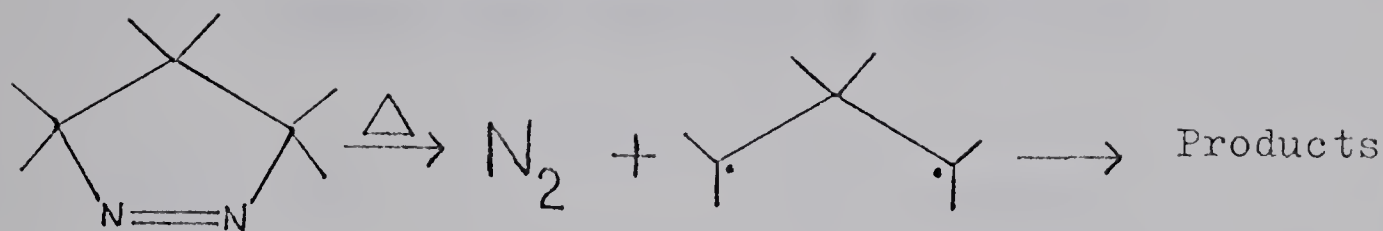
It must be postulated that trimethylene diradical is formed, and it has sufficient excess energy to lose a hydrogen atom, always from the central carbon (which is to be expected). Clearly then, these results cannot be explained by Bell's proposal in which all three carbon atoms in the intermediate are indistinguishable from each other.

(c) Trimethylene as an Intermediate in Pyrazoline Decomposition

Trimethylene 1,3-diradicals have been proposed as a discrete intermediate in the thermal decomposition of 1-pyrazolines*. Crawford and Mishra^{22a} have presented evidence that 1-pyrazolines must decompose via a diradical (Scheme XI). They found this necessary on the basis of kinetics and product distribution.

*Again the term "diradical" here does not necessarily mean that proposed by Benson, but is more in line with what Hoffmann defines as the trimethylene intermediate.

SCHEME XI

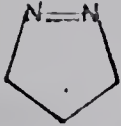


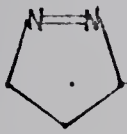







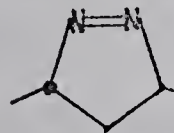




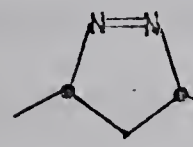
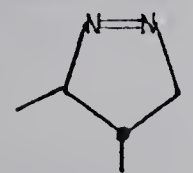
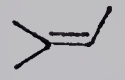
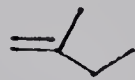

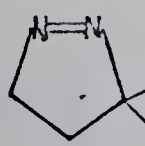


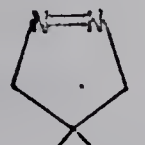
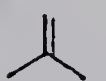


Furthermore, they propose that the diradical in this case is not a true diradical to the extent that the electron on each end is not completely free of the influence of the other. So instead of having a pair of spectroscopic doublets, the intermediate would be best described as a singlet. Product distributions for the thermolysis of some 1-pyrazolines are given in Table 10.

The butenes formed from 2 give rise to the following ratio: cis- + trans-2-butene/1-butene = 0.84. This may be compared with previous values of 0.95¹¹ and 1.02¹² obtained from the thermal isomerization of methylcyclopropane. Also, there is an absence of isobutene from 2 and the absence of any butenes other than isobutene from 3. This implies that once the cyclopropane is formed it does not possess sufficient energy to isomerize, and hence, the initial step in the thermal decomposition of 1-pyrazolines cannot be concerted expulsion of nitrogen, with the simultaneous formation of a cyclopropane. In the decomposition of 8, it should be noted that the formation of 2-methyl-1-butene (trace) requires a 1,4-hydrogen migration, similar to that proposed by Bader and Generosa to explain the formation of 3-methyl-1-butene in the reaction of triplet methylene with cis-2-butene.

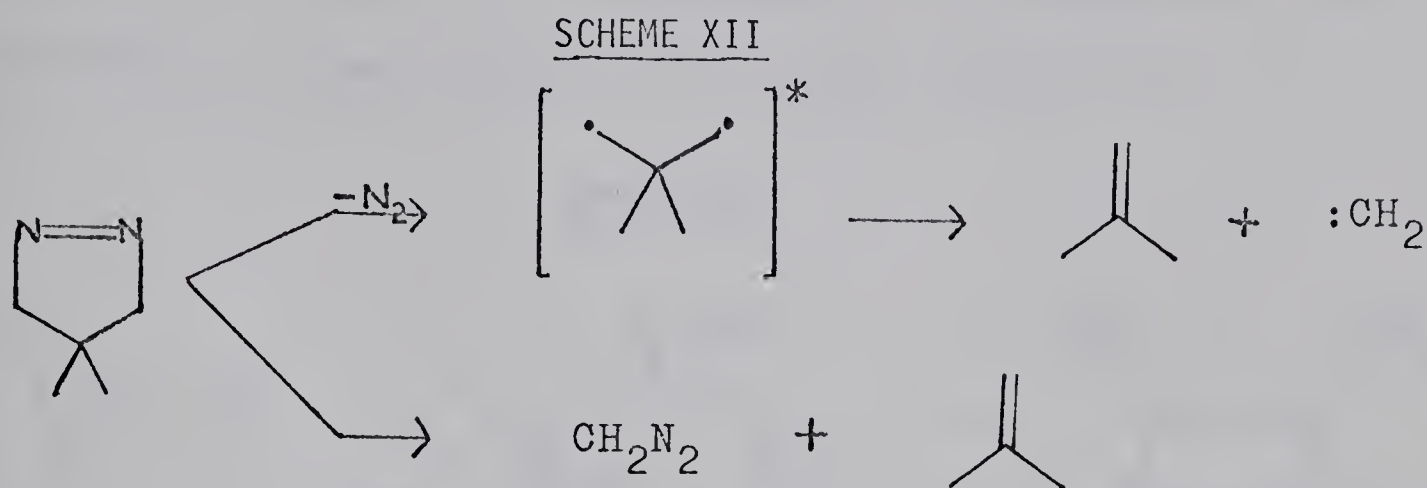
TABLE 10

PRODUCTS FROM THERMOLYSIS OF 1-PYRAZOLINES

1-Pyrazoline ^a	Product %			
 (1)	 89.2	 10.8		
 (2)	 93.3	 3.7	 1.2	 1.9
 (3)	 52.3	 47.7		
 (4)	 25.4	 72.6	 0.9	 1.1
 (5)	" 66.1	" 33.2	" 0	" 0.7
 (6)	" 21.8	" 46.0	 16.3	 15.8
 (7)	" 35.2	" 43.7	" 14.4	" 7.12
 (8)	 96.7	 1.5	" 1.8	" trace
 (9)	" 98.6	 1.4		" trace

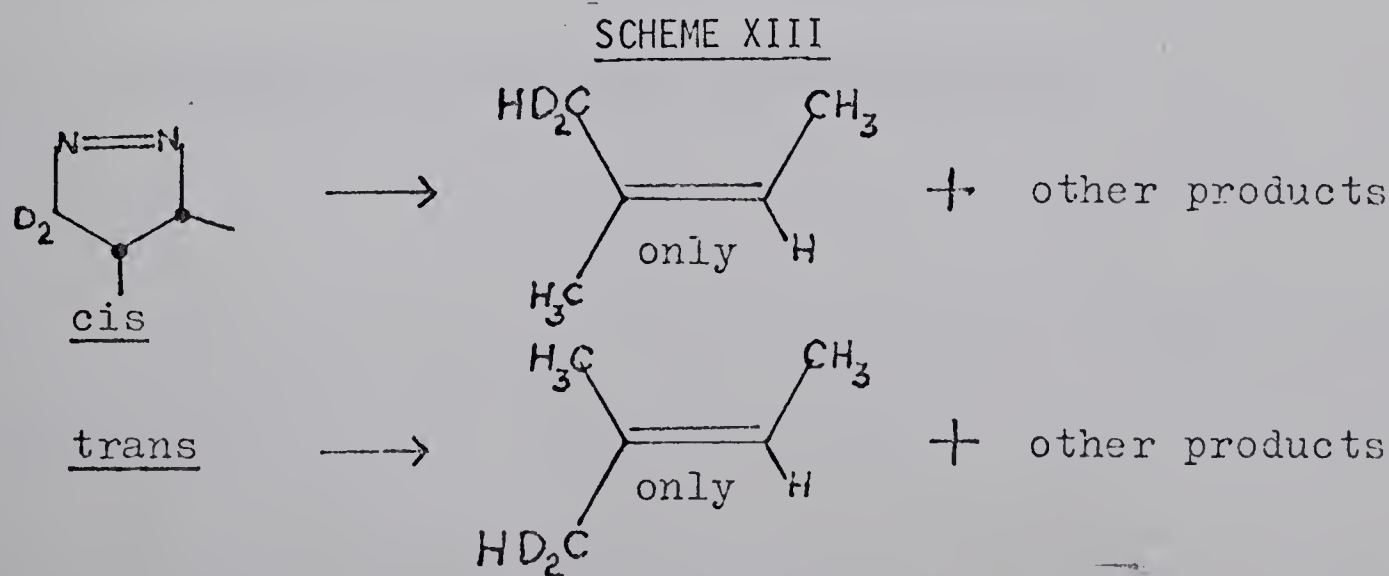
^aAll runs at 100-200 mm; ^bRef. 22b.

Pyrazoline 9 gives rise to two unexpected products. The 2-methyl-1-butene formed (trace) requires a 1,2-methyl shift for its formation and the isobutene may arise from either of two pathways:



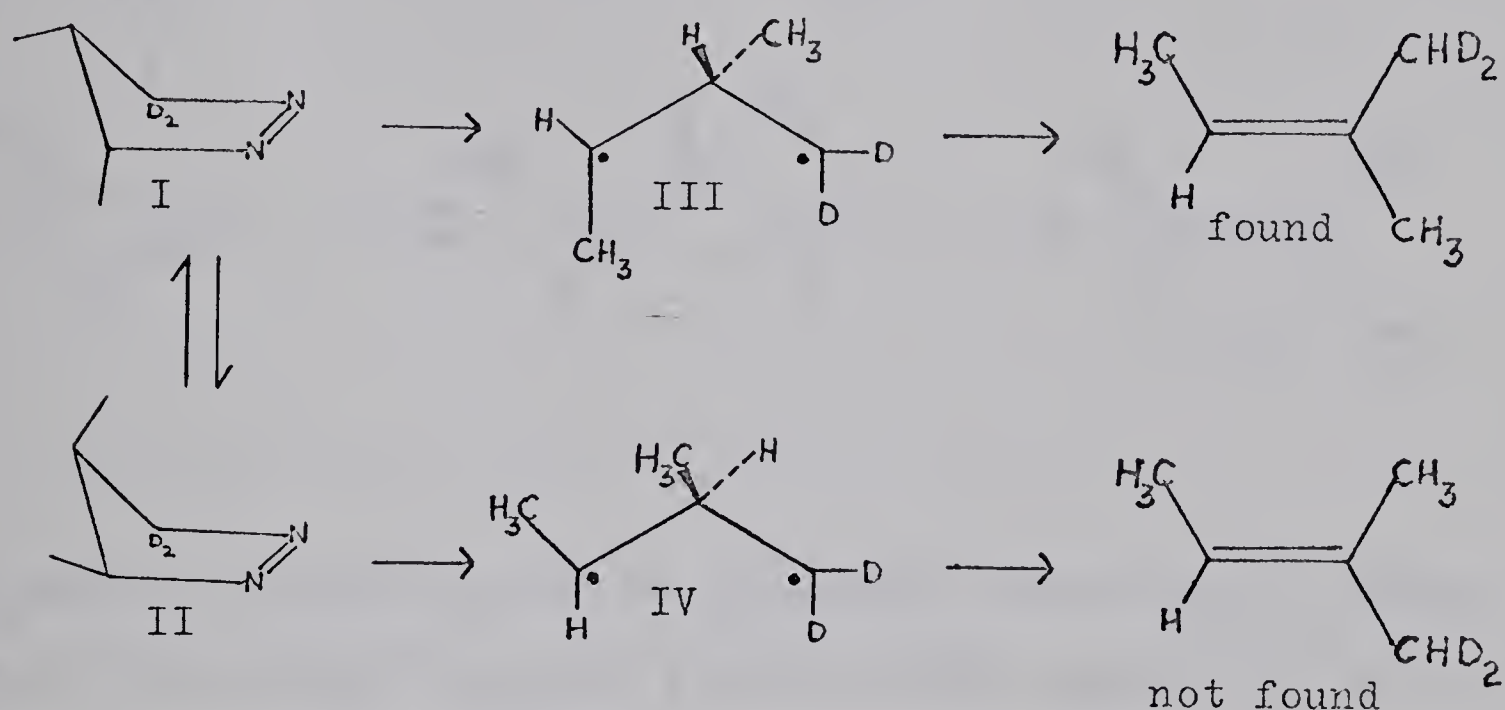
It is impossible to determine from the data which of the two pathways is operating. Crawford and Mishra conclude, "the products of pyrolysis of cyclopropanes indicate a quantitative similarity with those obtained by pyrazoline thermolysis and supports the geometry of the intermediate suggested as being a reasonable species in such reactions as cyclopropane and pyrazoline thermolysis and for the addition of methylene species to olefins."

Ali^{22b} has also studied the decomposition of cis- and trans-3,4-dimethyl-5,5-dideuterio-1-pyrazoline and determined the position of the deuterium in the 2-methyl-2-butene produced:-



This implies that both isomers decompose via preferred transition states and that the intermediate diradical has a preferred conformation in each case. First, let us examine the cis-isomer, it has two conformations and from what is known of the stereochemistry of ring compounds, one should not be very much favored over the other (Scheme XIV).

SCHEME XIV

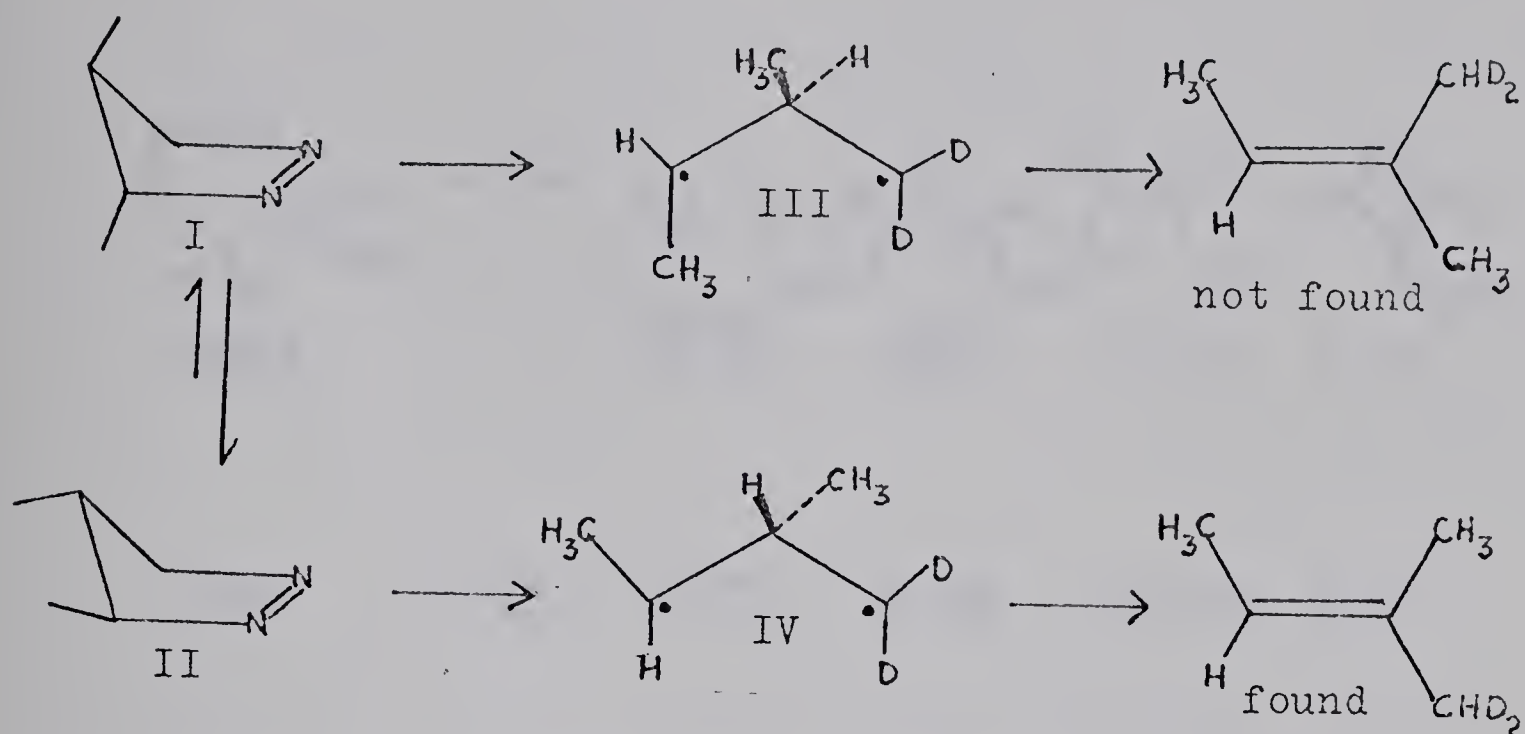


Obviously, the 2-methyl-2-butene is coming from a diradical of conformation III, and quite probably this arises from the pyrazoline conformer I.

This is in accordance with the suggestion of Crawford and Mishra that the preferred conformation for the thermolysis process is that wherein the bulky substituent on C_4 is in a pseudo-equatorial position.

In the case of the trans-pyrazoline we have,

SCHEME XV

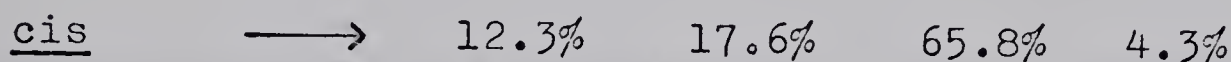
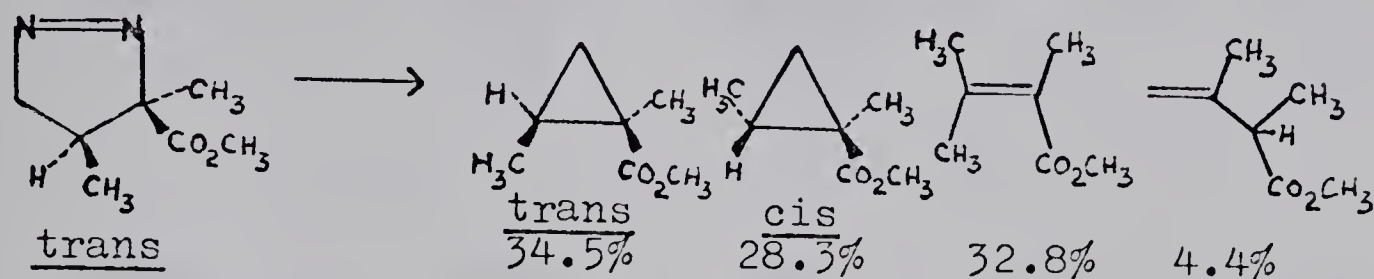


It would be expected here that the diequatorial conformation, II, would be the favored one. The product 2-methyl-2-butene supports this and can only arise from the diradical IV.

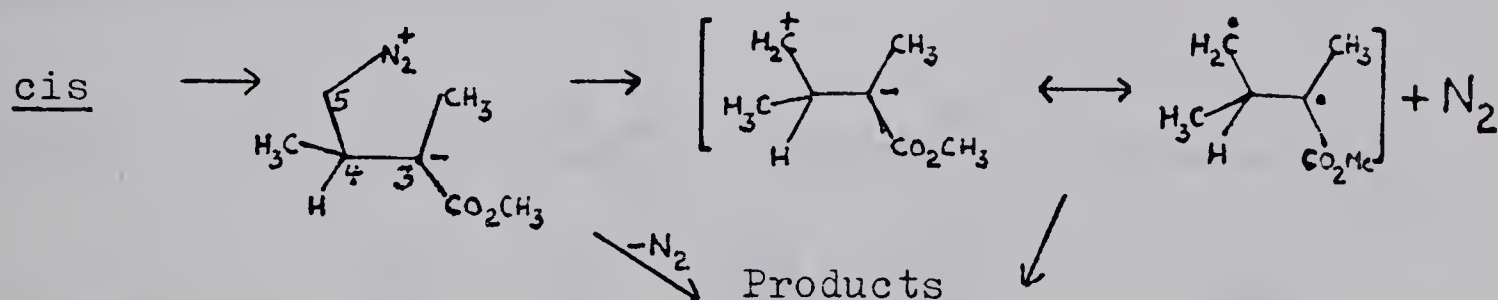
The pyrazolines cis- and trans-4-deuterio-3-methyl-1-pyrazoline were decomposed thermally by Erickson^{22c}. It was found that in this case the cis- and trans-2-deuteriomethylcyclopropane were present in equal amounts which is in contrast with Ali's results for the dimethylpyrazoline where the cis-DMCP was preferred for both the cis- and trans-starting material. Obviously, there are some subtle interactions at work in the intermediate diradical which influence the isomer ratio of the cyclopropanes.

Other workers have also decomposed pyrazolines both thermally^{24,25a,b,c} and photochemically^{23,26}. VanAuken and Rinehart²⁴ obtained the following

product distribution when they thermally decomposed cis- and trans-3,5-dimethyl-3-carbomethoxy-1-pyrazoline:

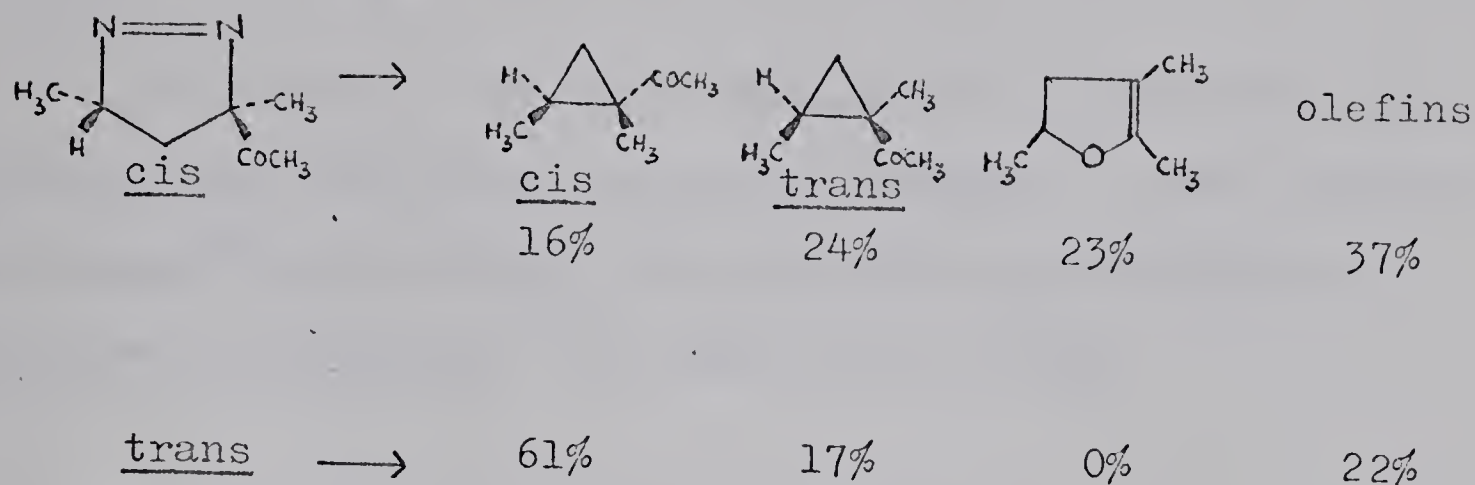


The mechanism proposed in this case was as follows:

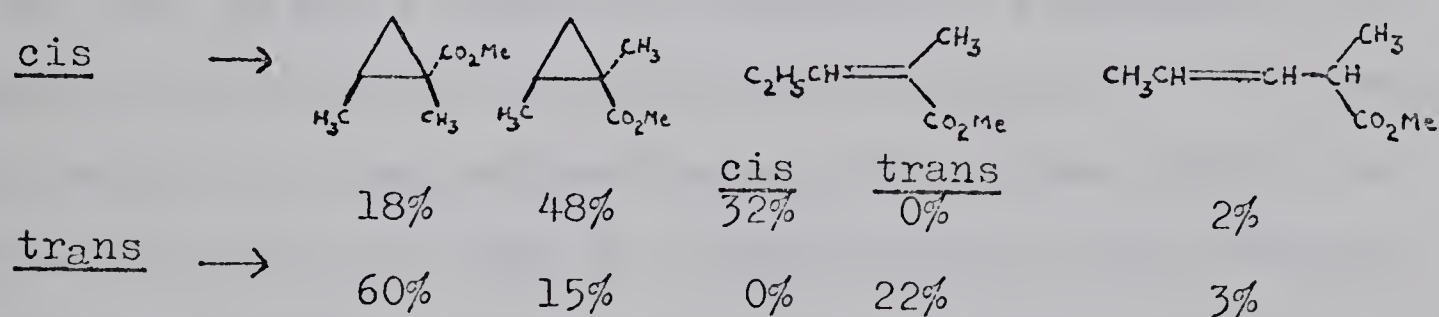


The dipolar intermediate suggested here should, in specific cases, give rise to alkyl migration from C₄ to C₅. In addition to this, the negative charge developed on C₃ should delocalize onto a suitable neighboring carbonyl group and result in dihydrofuran being formed. McGreer et al.^{25a}, have observed products resulting from alkyl migration when they decomposed 3-cyano-3-carbomethoxy-4,4-dialkyl-1-pyrazolines. They concluded that alkyl migration is concerted with the loss of nitrogen.

McGreer and co-workers²⁵ have also decomposed cis- and trans-3,5-dimethyl-3-acetyl-1-pyrazoline and obtained the following results,



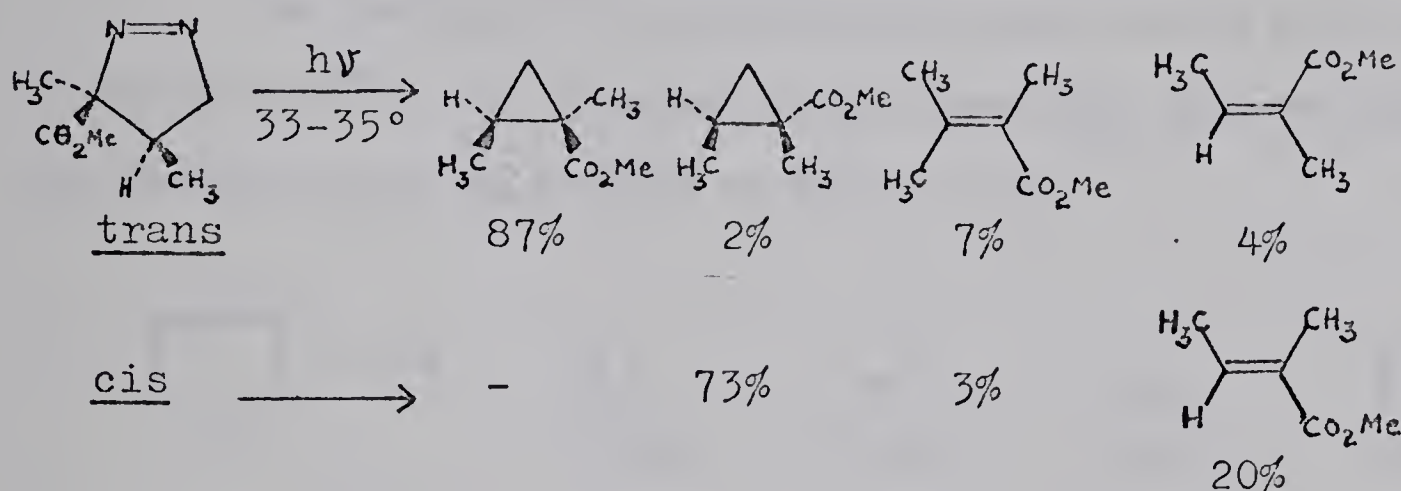
In this case where we have a suitable carbonyl group, we see the dihydrofuran, but only in the case of the cis-pyrazoline. If the acetyl group is now replaced by a carbomethoxy group, then the product distribution is as follows,



All of the foregoing were carried out in solution and it is quite possible that an ionic mechanism may operate, in contrast to Crawford and Mishra's gas phase work where a 1,3-diradical mechanism is undoubtedly operating. McGreer et al.^{25b} also thermolyzed the foregoing pyrazolines in the gas phase and found that the stereochemical reversal shown by the cyclopropane products was increased. He concluded that there may be a different

mechanism (or at least an additional one) operating in the solution phase from that of the gas phase.

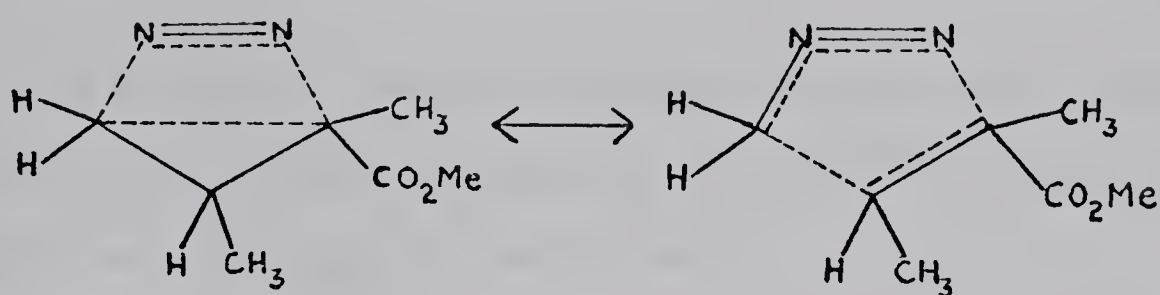
In contrast to the thermal decomposition of pyrazolines, very little has been done on their photochemical behavior. In 1960, VanAuken and Rinehart²³ photolyzed cis- and trans-3,4-dimethyl-3-carbomethoxy-1-pyrazoline in the solution. The results are as follows:



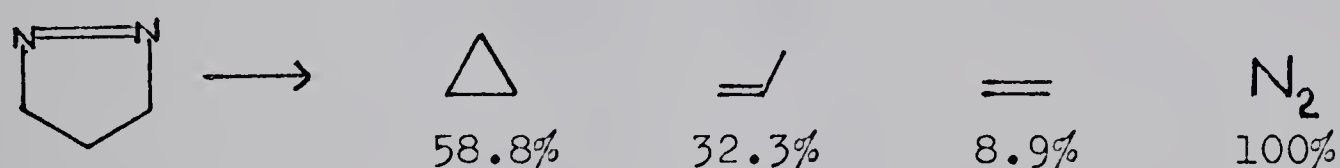
In this case, we have a remarkable preservation of stereochemistry as opposed to the results of 3,5-disubstituted-1-pyrazolines. If we compare these results with those obtained thermally for the same compounds, we notice that in this case there is a large decrease in olefin formation and the stereochemistry is preserved to a much greater extent in the cyclopropane products.

Another interesting feature of the above results is the appearance of an apparent cleavage product resulting from the loss of a carbon atom from the carbon skeleton. The resulting olefin in this process completely retains the geometry of the starting pyrazoline. The stereospecificity of the cyclopropanes and the cleavage products led the

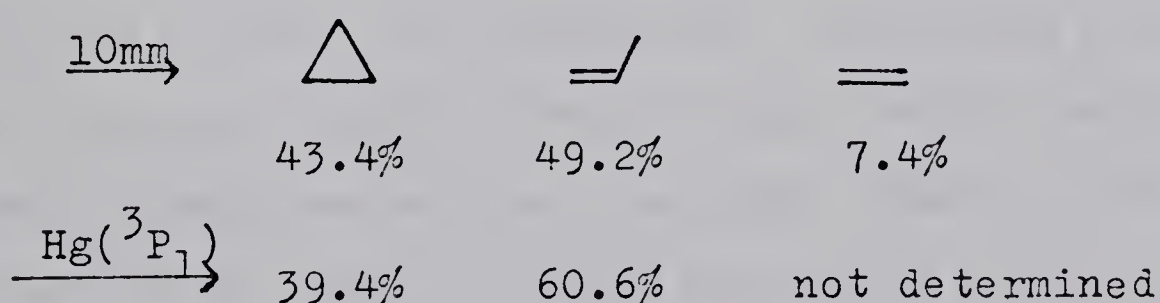
authors to propose the following transition state for the photochemical reaction:



The photolysis of 1-pyrazoline has been carried out in the gas phase by Kozak²⁶. The following products were found when the photolysis was carried out in the presence of 600 mm. of N₂:



At low pressures (vapor pressure of 1-pyrazoline)



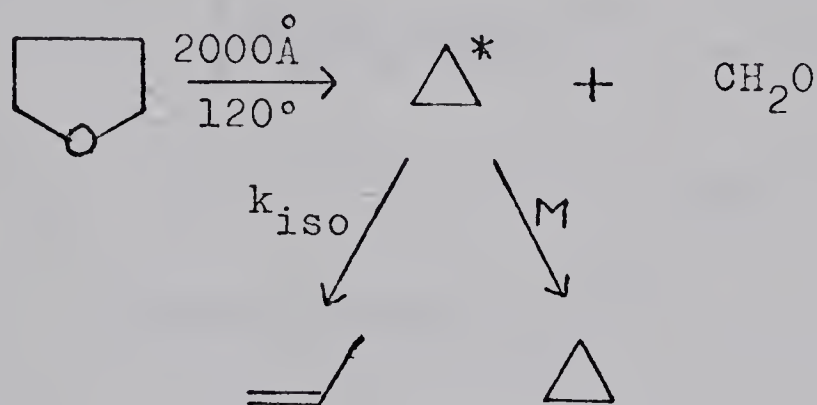
Again, in this case there is a product (ethylene) resulting from either cleavage of an intermediate diradical or from the loss of diazomethane in the starting material. The fragmentation appeared to practically be pressure independent.

The intermediate diradical could not be trapped using cis-2-butene

Also, the addition of oxygen or nitric oxide had very little effect on the product distribution. This then supports the conclusion of Benson that the lifetime of the trimethylene diradical is extremely short.

A supposedly somewhat analogous reaction to the decomposition of 1-pyrazolines has been performed by Roquitte²⁹. He photolyzed tetrahydrofuran and proposed the following:

SCHEME XVI

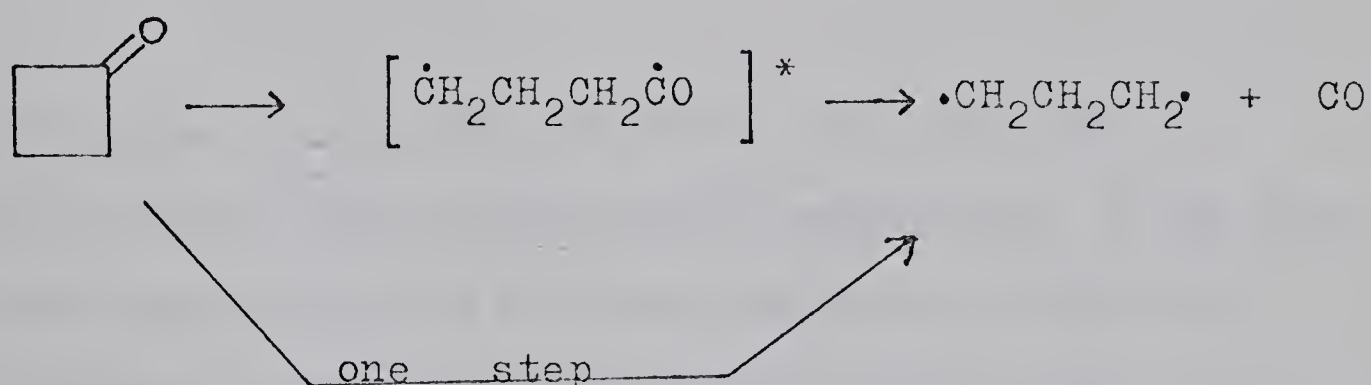


It was found that the high pressure limiting yield of cyclopropane/ cyclopropane + propylene was 0.72. He found that pressures over 150 mm. were sufficient to attain the limiting yield. He therefore proposed that the cyclopropane initially formed is a much 'cooler' species than that formed from methylene addition to ethylene. However, he did not take into account the probable increased deactivation efficiency of tetrahydrofuran over ethylene. A simple calculation of the excess energy content of the initially formed cyclopropane yielded a value of 86 kcal./mole. The author, however, makes no mention of a trimethylene diradical and states that the primary process is the formation of a 'hot' cyclopropane.

(d) Trimethylene as an Intermediate in Cyclobutanone Photolysis

The photolysis of cyclobutanone^{30,31a,b,32} may also give rise to a 1,3-diradical, but this is still in dispute. Srinivasan^{31a,b} has favored a concerted process while others have favored a diradical process. The trimethylene diradical may arise by either of two processes:

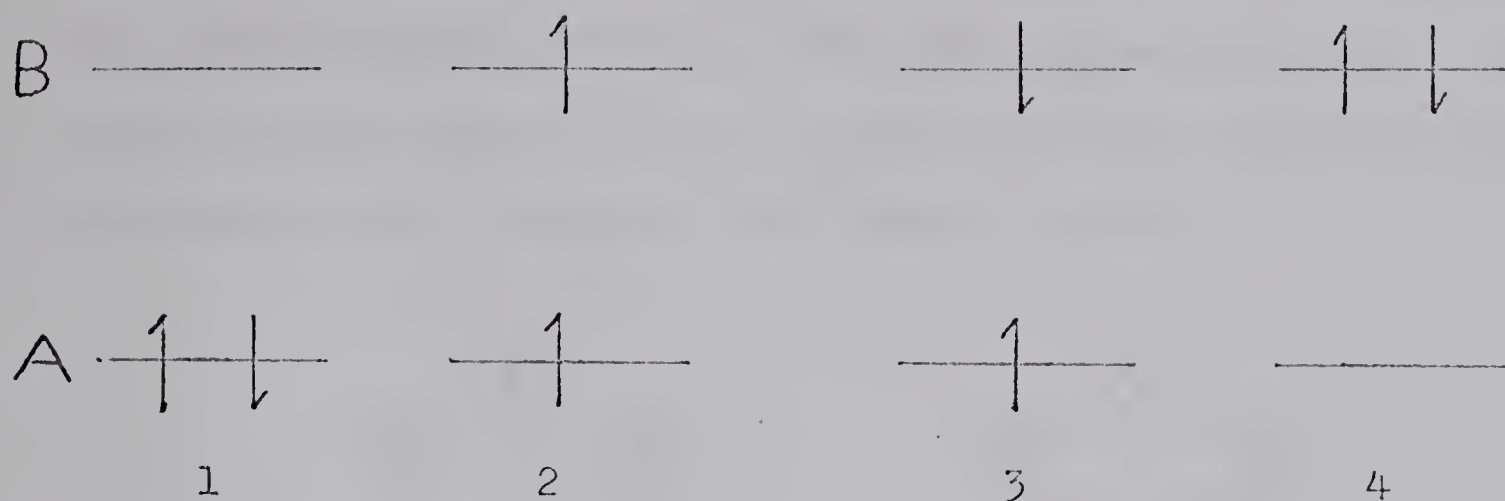
SCHEME XVII



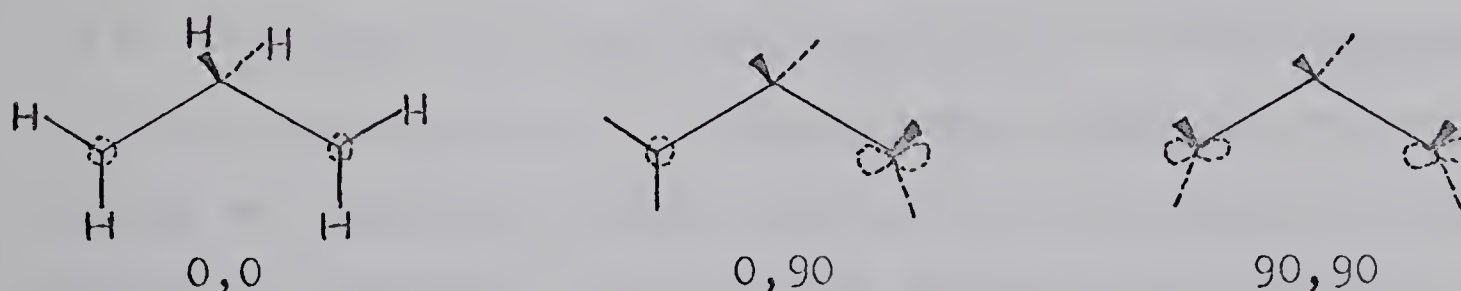
Klemm et al.³², have found that the ratio of cyclopropane to propylene appeared to rise to a value around 30 at 160 mm. of substrate using 3130 Å light at 100°C. But using 2537 Å the same ratio appeared to tend towards 4 when 300 mm. of substrate was used. This ratio difference may reflect different mechanisms or merely that the cyclopropane formed at 2537 Å is much 'hotter' than that formed at 3130 Å.

(e) Theoretical Treatment of Trimethylene

A recent paper by Hoffmann³³ treats the trimethylene diradical from a theoretical aspect using extended Hückel calculations. He calculates that the trimethylene diradical has two energy levels close in energy and for two electrons occupying these four possible states arise:

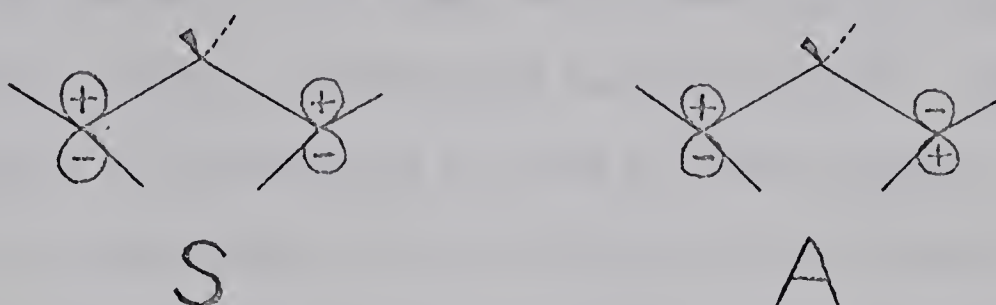


The possibility that state 2 (triplet) is the true ground state is mentioned but does not have any effect on the calculations. On the basis of the spatial part of the wave functions, the author concludes that state 1 will have a barrier to internal rotation, while states 2 and 3 will be very 'floppy' entities with a low barrier to internal rotation. Three arrangements for the terminal $-CH_2$ groups are considered:



The author calculated that the potential energy surface for state 1 had a fairly sharp energy well for the 0,0 configuration with the minimum at a CCC angle of 125° . The 90,90 configuration displayed no well but decreased to a low value as the angle became smaller, leading to cyclopropane. States 2 and 3 showed only very broad energy wells for all

three configurations. The trimethylene intermediate is then defined as the 0,0 configuration of state 1 with a CCC bond angle of 125° . Furthermore, the most stable state for an angle of 125° was calculated to be antisymmetric (A), as opposed to a symmetric one (S).



The consequence of this is that the species with two electrons in the lower (A) level should prefer to close to cyclopropane in a conrotatory manner. This is precisely what is observed when cis- and trans-3,5-dimethyl-1-pyrazoline is thermally decomposed.

Hoffmann also treated the addition of methylene to ethylene. It was concluded in this case that the addition of singlet methylene, while initially unsymmetrical, is a concerted process which does not proceed through an intermediate, and the addition of triplet methylene proceeds through an intermediate. To reach this conclusion, no account was taken of the spin state of the methylene, but merely the methylene geometry and the spatial part of the wave functions.

CHAPTER II

PROPOSAL

The thermolysis of simple methyl substituted 1-pyrazolines almost certainly produces trimethylene 1,3-diradicals²². Furthermore, these diradicals are potentially the same as those produced in, (a) the thermolysis of cyclopropanes, (b) the addition of methylene to olefinic double bonds, (c) the photolysis of cyclobutanone, and, (d) the photosensitized decomposition of 1,2-dimethylcyclopropane. Because of this, it was decided to investigate the photochemical decomposition of some methyl substituted 1-pyrazolines under a variety of conditions; namely, direct photolysis in gas phase with and without added inert gas, direct photolysis in solution, and benzophenone photosensitized photolysis, which would presumably yield a triplet diradical.

The photochemical decomposition may give rise to a diradical containing more excess energy than that produced thermally. The products resulting from the diradical could then be studied and correlated with the product distributions from other possible sources of trimethylene.

When methylene reacts with C_n olefins, the C_{n+1} olefins may arise from three different sources; 1) from direct insertion of methylene into a C-H bond, 2) from the rearrangement of a trimethylene diradical, and 3) from the isomerization of a 'hot' cyclopropane. When pyrazolines are decomposed source 1 is eliminated and source 3 may be quenched at high pressures or in solution. This leaves 2 as the only

source of olefin in pyrazoline decomposition at high pressures or in solution; and 2 and 3 as the only sources at low pressures.

A particularly intriguing product in the reaction of triplet methylene with cis-2-butene is 3-methyl-1-butene. It has been proposed that it arises from a 1,4-hydrogen migration^{13k} (Scheme VII). If this migration occurs before spin inversion in the diradical, then a triplet olefin must be produced. This implies that the system has sufficient energy to produce a triplet olefin. If such is the case, then why are not the olefins (2-methyl-1-butene and 2-methyl-2-butene) which result from a 1,2-hydrogen migration produced in the triplet reaction? Again, if the migration occurs after triplet to singlet conversion, why are not 1,2-hydrogen migrations observed? Also, 3-ethyl-1-butene is not formed (or only to a very small extent) in the normal singlet methylene plus cis-2-butene reaction except at very low pressures, where it is believed to arise from a highly energized singlet diradical. In any case, it is difficult to visualize a 1,4-hydrogen migration without an accompanying 1,2 migration. An alternate source for 3-methyl-1-butene is from an abstraction-recombination mechanism (Scheme VIII). By photosensitizing cis- and trans-3,4-dimethyl-1-pyrazoline using benzophenone as the sensitizer, it was hoped to determine whether 3-methyl-1-butene arises from a triplet diradical or some other source.

By comparing relative olefin yields in pyrazoline photolysis to those from the thermal isomerization of cyclopropanes, it may be possible to support (but not prove) a diradical mechanism for such isomerizations.

It was also hoped that comparing gas phase photolysis with solution phase will help establish whether the same mechanism is operative in both cases. It has been suggested²⁵ that in the thermolysis of some pyrazolines, a different or additional mechanism is operating in the condensed phase.

By observing the cyclopropanes and olefins from pyrazoline photolysis, it should be possible to support or refute Hoffmann's theory concerning the nature of the trimethylene intermediate. His theory is supported by the results of Crawford and Mishra^{22a} from the thermolysis of pyrazolines where conrotation would primarily account for the isomeric distribution of the cyclopropanes. By photosensitizing the pyrazolines, it should also be possible to determine whether the triplet diradical is a 'floppy' molecule as Hoffmann suggests.

It was hoped to determine where and when a trimethylene diradical is formed, its triplet and singlet properties, and to interpret the similarities and differences between trimethylene from 1-pyrazolines and that which has been suggested to occur in other systems.

An examination of the cleavage products resulting from pyrazoline decomposition is also desirable to determine if they arise from a 'hot' intermediate, or if the mechanism proposed by Rinehart and VanAuken²³ is more probable. The stereospecificity of the formation of the cleavage product in the work of Rinehart and VanAuken would seem to leave little alternative to a concerted mechanism.

CHAPTER III

RESULTS AND DISCUSSION

(A) Results

Seven different 1-pyrazolines have been photolyzed under a variety of conditions using light 3000 Å (all 1-pyrazolines absorb around 3200 Å). Five of the pyrazolines, 1-pyrazoline(1); 3-methyl-1-pyrazoline(2); 4-methyl-1-pyrazoline(3); trans-3,5-dimethyl-1-pyrazoline(4); and cis-3,5-dimethyl-1-pyrazoline(5), were prepared according to the method of Mishra^{22d} from the appropriate 1,3-dibromides and hydrazine followed by oxidation. The trans-3,4-dimethyl-1-pyrazoline(6), and the cis-3,4-dimethyl-1-pyrazoline(7), were prepared by the procedure of Ali^{22b} by the addition of diazomethane to trans- and cis-2-butene respectively.

All pyrazolines were photolyzed in the gas phase at low pressures (5-10 mm) and at higher pressures (600 mm nitrogen added). Pyrazolines 1, 4, 5, 6 and 7 were also decomposed in 95% ethanol both by direct photolysis and benzophenone photosensitization. The latter presumably gives rise to a triplet intermediate. Pyrazolines 4, 5 and 7 were also photolyzed at 77°K and 1 was photolyzed in tetramethylethylene solvent in addition to ethanol.

Product analyses were carried out using gas chromatography (gc) and all peaks were verified by comparison with authentic samples. In some cases, two different columns were used. Where doubt existed, the correct structures were verified by mass spectrometry after trapping the compound in question.

TABLE 11
PHOTOLYSIS OF 1-PYRAZOLINE (1)

Run No.	Photolysis Method	Pressure Torr.	Products, mole %				
			N ₂	Cyclo-C ₃ H ₆	C ₃ H ₆	C ₂ H ₄	Cyclo-C ₃ H ₆ /C ₃ H ₆
1	Direct	9	97.5	42.2	53.5	2 - 3	0.789
2	Direct	9	97.2	43.0	52.8	2 - 3	0.815
3	Direct	11	98.0	45.6	50.3	2 - 3	0.905
4	Direct	600 (N ₂)	--	61.9	34.8	2 - 3	1.78
5	Direct	Soln. EtOH	--	90.6	9.4	<1	9.65
6	Direct	Soln. EtOH	--	90.0	10.0	<1	9.00
7	Direct ^a	Soln. TME	--	85	15	8-9(TMCP) ^b	5.67
8	Photosens	EtOH	--	87.7	12.3	1	7.13
9	Photosens	EtOH	--	89.8	10.2	1	8.80
	Thermal ^{22a}	100 - 200	100	89.2	10.8	0	8.26

^aRun in solution of tetramethylethylene (TME); ^bTMCP = 1,1,2,2-tetramethylcyclopropane

The results for the photolysis of 1-pyrazoline(1) are given in Table 11. For the gas phase photolyses at low pressures about one to two percent of the reaction product was unidentified hydrocarbons. The yield of ethylene is believed to be too small²⁶ due to two factors: 1) the ethylene peak in the gc overlapped with the cyclopropane and an accurate measurement was impossible; and 2) some of the ethylene invariably gets pumped away when the nitrogen is being removed. When ethanol is used as the solvent, a small amount of a compound having the same retention time as methylethyl ether was detected.

Because the photosensitized reaction was carried out in ethanol, large quantities of acetaldehyde were also formed. This is to be expected since alcohols are known to be photochemically oxidized to corresponding carbonyl compounds in the presence of benzophenone. Another possible route for the formation of acetaldehyde is through the abstraction of a hydrogen atom from ethanol by the triplet diradical. This process should give rise to saturated hydrocarbons (other than cyclopropanes). No saturated hydrocarbons could be detected in any of the liquid phase photolyses.

To rule out the possibility of the triplet or singlet diradical reacting with ethanol to yield undetectable products, mass balances (nitrogen vs. hydrocarbons) were determined for two photosensitized runs and one direct photolysis run with 5. It was found that the nitrogen balanced, within experimental error, with the hydrocarbons in every case.

Direct photolysis of the pyrazolines in ethanol produced only trace amounts ($\sim 0.1\%$) of acetaldehyde. Photolysis of ethanol alone also produced trace amounts of acetaldehyde.

The results for the photolysis of 3-methyl-(2) and 4-methyl-1-pyrazoline(3), are listed in Table 12. In this case the 1-butene and the cis-2-butene were not completely resolved in the gc. The amount of each was estimated from the peak height after determining the total area of the two peaks.







Tables 13, 14, 15 and 16 give the product distributions for trans-(4) and cis-3,5-dimethyl-1-pyrazoline(5) photolysis. It should be pointed out here that the trans compound was essentially pure, while the cis contained 15% trans, as determined 100 mc nmr. The product yields given for 5 are corrected for the 15% of 4 present. No interconversion of 4 to 5 could be detected in either the gas or liquid phase photolysis.

In order to make a simple correction for the 15% of 4 in 5, they must decompose at comparable rates. Since no actual kinetic runs were done, three runs on each compound were performed and the total amount of product for equivalent times was determined by use of a Toepler pump. As can be seen, the rates of decomposition are comparable so the correction may be made directly (Table 17, Page 55).

In Tables 14 and 16, the yields of ethylene and propylene are not very accurate for the photolyses in ethanol solution. In these runs, after irradiation the solutions were first run through a column of 20% carbowax 1500 on Diatoport and the hydrocarbon products were collected by passing the effluent gas through a spiral trap cooled to 77°K. This method was found to trap very little of the ethylene and only about one third to one half of the propylene. All higher hydrocarbons were

TABLE 12








PHOTOLYSIS OF 3-METHYL(2) AND 4-METHYL-1-PYRAZOLINE(3)

Run No.	Photolysis Method	Pressure Torr.	C ₂ H ₄	Product, mole %					
									
2									
1	Direct	7 - 8	2.8	69.4	2.50	~9	~10	0.91	
2	Direct	7 - 8	2.6	71.3	1.93	~8	~9.5	0.66	
3	Direct	600 (N ₂)	2.2	78.7	0.4	~6.5	~7	trace ^a	
4	Direct	600 (N ₂)	2.2	79.4	0.6	5.5-6	6-6.5	trace	
	Thermal ^{22a}	100-200	0	93.3	1.16	1.9	3.7	0	
	Thermal ^{22c}		0	92.5	1.3	2.4	3.8	0	
3									
1	Direct	7 - 8	-	55.2	2.9	~4	6	20.6	
2	Direct	7 - 8	-	55.6	2.5	~3.5	~5.5	21.5	
3	Direct	600 (N ₂)	-	66.6	0.18	~0.8	~1	21.6	
4	Direct	600 (N ₂)	-	67.5	0.11	~0.8	~1	21.0	
	Thermal ^{22a}	100-200	-	52.3	0	0	0	47.7	

^a "Trace" may be taken as less than 0.1%.

TABLE 13

GAS PHASE PHOTOLYSIS OF TRANS-3,5-DIMETHYL-1-PYRAZOLINE(4)

Run No.	Time, min.	Pressure, Torr.	Product, mole %							
									C ₂ H ₄	
1	60	5 - 6	26.7	58.6	2.2	2.9	?	~0.2	8.1	9.6
2	60	5 - 6	26.4	60.1	2.3	3.3	?	~0.1	6.1	7.9
3 ^b	60	5 - 6	27.2	60.4	2.3	3.0	?	~0.1	4.0	7.4
4	120	5 - 6	27.7	58.4	2.2	2.9	?	0.1-0.2	8.2	8.9
5	120	5 - 6	25.1	61.5	2.4	3.0	?	~0.1	8.2	7.6
6	120	5 - 6	25.8	61.1	2.2	3.2	?	0.1-0.2	6.5	7.6
7	120	5 - 6	26.2	59.0	2.0	3.0	?	0.1-0.2	10.1	9.9
8	60	60 (N ₂)	24.9	62.5	1.9	2.9	?	0	6.3	7.8
9	60	60 (N ₂)	27.3	58.5	1.8	2.5	?	0	7.5	9.8
10	240	120 (N ₂)	24.7	63.4	1.9	3.0	0	0	6.2	7.0
11	60	600 (N ₂)	24.7	61.9	2.1	3.3	0	0	6.1	8.0
12	120	600 (N ₂)	24.9	61.1	2.2	3.2	0	0	7.0	8.6
Thermal ^{22a}		100-200	25.4	72.6	1.08	0.92	0	0	0	0

^aPartially hidden under trans-2-pentene peak in gc; ^bunfiltered light.

TABLE 14

LIQUID PHASE PHOTOLYSIS OF TRANS-3,5-DIMETHYL-1-PYRAZOLINE(4)

Run No.	Time, min.	Photolysis Method	Product, mole %					
1 ^a	60	Direct	43.9	42.3	3.0	4.2	trace	6.6 0
2 ^a	120	Direct	43.7	42.6	2.5	4.5	trace	6.8 0
3 ^a	270	Direct	44.6	41.5	2.8	4.4	1.6	6.7 0
4	60	Direct	44.5	43.2	2.9	4.8	trace	3.3 ~1.2
5	120	Direct	46.6	43.9	2.2	4.2	trace	3.0 ~1
6	120	Direct	44.6	45.0	3.4	3.6	trace	2.4 ~1
7	180	Direct	45.2	43.9	3.0	4.1	~0.2	3.1 ~1
8	60	Photosens	60.4	39.6	trace	trace	0	trace trace
9	180	Photosens	62.3	37.7	trace	trace	0	trace trace
10	180	Photosens	60.9	39.1	trace	trace	0	trace trace
11 ^b	210	Direct	50.6	37.4	5.6	5.6	trace	~0.9 0

^aNeat liquid, all others run in 95% EtOH; ^b77°K.

TABLE 15

GAS PHASE PHOTOLYSIS OF CIS-3,5-DIMETHYL-1-PYRAZOLINE(5)







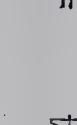






Run No.	Time, min.	Pressure, Torr.	Product, mole %									
										C ₂ H ₄		
1	15	5 - 6	42.5	47.1	1.1	1.0	?	~0.2	7.3	8.1		
2	30	5 - 6	42.1	47.7	1.0	0.9	?	~0.1	7.6	8.2		
3	60	5 - 6	43.6	45.4	1.3	1.1	?	~0.2	7.0	8.4		
4	60	5 - 6	41.7	48.1	1.0	0.9	?	~0.2	6.7	8.1		
5	60	5 - 6	40.9	48.7	1.0	0.9	?	~0.1	8.1	8.4		
6	195	5 - 6	41.3	48.0	1.2	0.9	?	~0.1	7.1	8.5		
7	60	600(N ₂)	40.8	48.9	0.3	0.3	0	0	6.6	9.8		
8	60	600(N ₂)	41.3	48.9	0.2	0.4	0	0	5.8	9.3		
9	120	600(N ₂)	41.0	49.1	0.2	0.4	0	0	4.6	9.4		
Thermal ^{22a}		100-200	66.1	33.2	0.68	0	0	0	0	0		

TABLE 16

LIQUID PHASE PHOTOLYSIS OF CIS-3,5-DIMETHYL-1-PYRAZOLINE(5)

Run No.	Time, Min.	Photolysis Method	Product, mole %						
							C ₂ H ₄		Et ₂ O
1	60	Direct	61.6	33.5	1.0	0.4	trace	3.0	~2.5
2	60	Direct	61.3	33.9	1.1	0.5	trace	3.1	~2
3	60	Direct	62.1	34.5	0.9	0.6	trace	2.2	~2
4	180	Direct	61.5	34.3	1.0	0.4	trace	2.5	~2.5
5	600	Direct	61.8	34.0	1.5	0.8	~0.2	2.2	~2
6	60	Photosens.	58.7	40.5	<0.3	trace	0	~0.5	~1
7	60	Photosens.	60.1	38.9	<0.2	trace	0	~0.8	~0.5
8	120	Photosens.	60.4	39.3	<0.2	trace	0	~0.3	~0.5
9	120	Photosens.	59.3	39.8	<0.3	trace	0	~0.5	~0.5
10 ^a	600	Direct	56.4	39.1	3.0	trace	trace	1.5	~0.2

^a 77°K.

TABLE 17

TOTAL PRODUCT YIELDS FOR ONE HOUR IRRADIATION
OF CIS- AND TRANS-3,5-DIMETHYL-1-PYRAZOLINE

Product Pressure, Torr. ^a			
<u>cis-</u>		<u>trans-</u>	
Nitrogen	Hydrocarbon	Nitrogen	Hydrocarbon
142.0	146.5	161.0	165.0
133.5	140.5	138.0	141.0
157.5	160.0	140.5	144.5







^aPressures are directly proportional to the number of moles. In each case 251 torr of product represents 100% reaction.

approximately eighty-five percent retained (see experimental section) and in the small loss that occurred, the C_4^1s were lost at no measurably faster rate than the C_5^1s . The runs done using neat liquid 4 were done directly in the vacuum rack and the products separated from the substrate by trap to trap distillation. This means that the yield of cleavage product in solution is closely represented by the percent propylene (6.7%) found in the neat liquid runs.

Tables 18 to 21 list the results obtained for the photolysis of trans-(6) and cis-3,4-dimethyl-1-pyrazoline(7). In this instance also, a peak appeared in the gc whose retention time corresponded with that of methylethyl ether. The percentages obtained for this compound are not very

TABLE 18




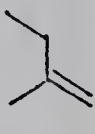
GAS PHASE PHOTOLYSIS OF TRANS-3,4-DIMETHYL-1-PYRAZOLINE(6)

Run No.	Time, min.	Pressure, Torr.	Product ^b , mole %					
								
1	30	5 - 6	37.4	24.4	?	0.3	16.5	14.7
2	30	5 - 6	36.9	24.5	?	0.3	16.5	14.5
3	60	5 - 6	37.7	24.5	?	<0.5	16.6	14.3
4	60	5 - 6	36.9	24.3	?	~0.4	16.4	14.6
5	60	55(N ₂)	39.3	24.7	?	trace	14.7	14.3
6	60	600(N ₂)	41.6	24.8	0	0	14.0	13.0
7	60	600(N ₂)	40.9	24.7	0	0	14.2	13.4
8	120	600(N ₂)	41.0	24.5	0	0	14.3	13.4
Thermal ^{22b}		100-200	21.8	46.0	0	0	16.3	15.8
								0

^aMostly hidden under 2-methyl-2-butene peak; ^bpropylene present in about 1% in all photolysis runs, ethylene present in about 0.7% in all photolysis runs.

TABLE 19








LIQUID PHASE PHOTOLYSIS OF TRANS-3,4-DIMETHYL-1-PYRAZOLINE(6)

Run No.	Time, min.	Photolysis Method	Product ^a , mole %				
							CH ₃ OC ₂ H ₅
1	120	Direct	50.7	13.0	18.3	14.1	2.98
2	180	Direct	49.3	13.5	19.2	14.2	3.02
3	240	Direct	48.1	13.6	19.7	15.1	3.24
4	240	Direct	48.2	13.2	19.4	15.0	3.12
5	120	Photosens.	72.7	22.8	~1.5	1.1	1.9
6	180	Photosens.	72.5	22.3	~1.8	1.4	1.7
7	240	Photosens.	72.4	22.4	~1.8	1.5	2.0

^aIn all these runs only traces of ethylene were detected, while propylene was always less than 0.5%.

TABLE 20




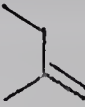

GAS PHASE PHOTOLYSIS OF CIS-3,4-DIMETHYL-1-PYRAZOLINE(7)

Run No.	Time, min.	Pressure, Torr.	Product ^a , mole %						
									
1	60	5 - 6	37.8	43.2	0.87	0.57	4.37	4.72	7.15
2	60	5 - 6	37.5	42.8	0.89	0.69	4.96	4.81	7.24
3	120	5 - 6	37.9	43.1	0.85	0.59	4.43	4.66	7.22
4	120	5 - 6	37.0	43.3	0.90	0.65	4.82	4.90	7.24
5	60	600(N ₂)	35.2	50.8	0	0	3.45	2.81	6.94
6	60	600(N ₂)	35.7	50.5	0	0	3.38	2.79	6.82
7	120	600(N ₂)	35.4	50.9	0	0	3.31	2.80	6.92
Thermal ^{22b}			35.2	43.7	0	0	14.4	7.12	0

^aIn all runs propylene accounted for ~1% and ethylene for ~0.9%.

TABLE 21

LIQUID PHASE PHOTOLYSIS OF CIS-3,4-DIMETHYL-1-PYRAZOLINE(7)

Run No.	Time, min.	Photolysis Method	Product ^a , mole %				
							
1	120	Direct	27.9	59.4	4.38	3.58	4.15
2	180	Direct	26.4	60.4	5.00	3.75	3.96
3	240	Direct	26.6	62.0	3.71	3.02	4.02
4	240	Direct	--	--	--	--	4.00
5	120	Photosens.	65.9	32.1	0.5	trace	1.5
6	180	Photosens.	66.2	31.9	0.6	trace	1.3
7	240	Photosens.	66.2	32.1	0.5	trace	1.3
8	240	Photosens.	66.0	33.0	0.3	trace	~1.0
9 ^b	150	Direct	46.1	40.2	7.1	6.5	2-3
							CH ₃ OC ₂ H ₅

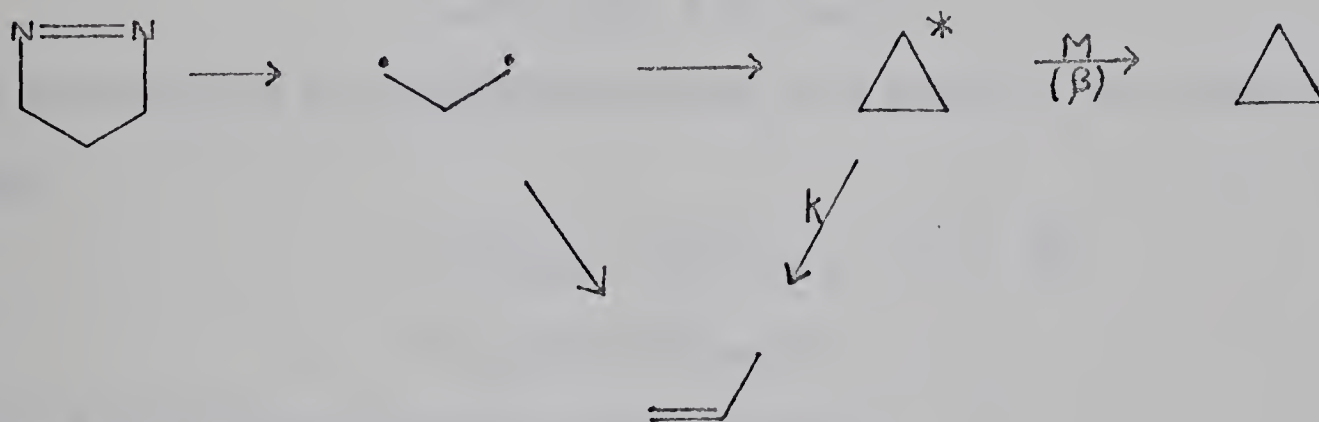
^aEthylene was not detected in any runs while propylene was always less than 0.7%; ^b77°k.

accurate since it was partially buried under the 2-methyl-2-butene peak.

(a) Estimation of the Excess Energy Content of the Initially Formed Cyclopropane in the Gas Phase Photolysis of 1-Pyrazoline.

One distinct feature of Table 11, Page 47, is the great pressure dependence of the cyclopropane to propylene ratio. This is consistent with the following reaction scheme:

SCHEME XVIII



From this pressure dependence we may make a rough evaluation of the excess energy content (E , Figure 1) of the 'hot' cyclopropane produced using the same approach as Roquette²⁹ and similar to that of Setser and Rabinovitch^{13f}.

The rate constant, k , for the isomerization of the 'hot' cyclopropane is given by

$$k = (P_i - P_\infty / \Delta_i) \beta \quad \dots\dots\dots \text{Eq. 1}$$

where P_i = propylene yield at pressure i

P_∞ = propylene yield at infinite pressure (solution)

Δ_i = cyclopropane yield at pressure i

and β = collision frequency of Δ^* (thermally excited cyclopropane)

The collision frequency, β , may be calculated from the following equation:

$$\beta = (8\pi kT/\mu)^{1/2} \sigma_{AB}^2 n_B$$

where k = Boltzman's constant

T = temperature in degrees Kelvin (300)

μ = the reduced mass of the system

$\sigma_{AB} = (\sigma_A + \sigma_B)/2$ - σ_A being the effective radius of the 'hot' cyclopropane and σ_B the effective radius of the deactivating species.

and n_B = number of deactivating molecules per cubic centimeter. At low pressure (~ 10 Torr),

$$\beta \approx 1.37 \times 10^8 \text{ sec.}^{-1}$$

By substituting the appropriate values from Table 10 into equation 1 we get,

$$\begin{aligned} k &= (53.2 - 10)/42.6 \times 1.37 \times 10^8 \\ &= 1.38 \times 10^8 \text{ sec.}^{-1} \end{aligned}$$

From Rice-Ramsperger-Kassel theory we have,

$$k = A(1 - E_a/E)^{s-1} \dots\dots\dots \text{Eq. 2}$$

where A = frequency factor for cyclopropane isomerization

E_a = activation energy for cyclopropane isomerization

E = excess energy (Figure 1) of the 'hot' cyclopropane

and s = the number of active vibrational modes in cyclopropane

Taking $s = 13$

$$E_a = 65 \text{ kcal/mole}$$

$$A = 10^{15.2}$$

and $k = 1.38 \times 10^8 \text{ sec.}^{-1}$

we obtain upon substituting into equation 2,

$$1.38 \times 10^8 = 10^{15.2} (1 - 65/E)^{12}$$

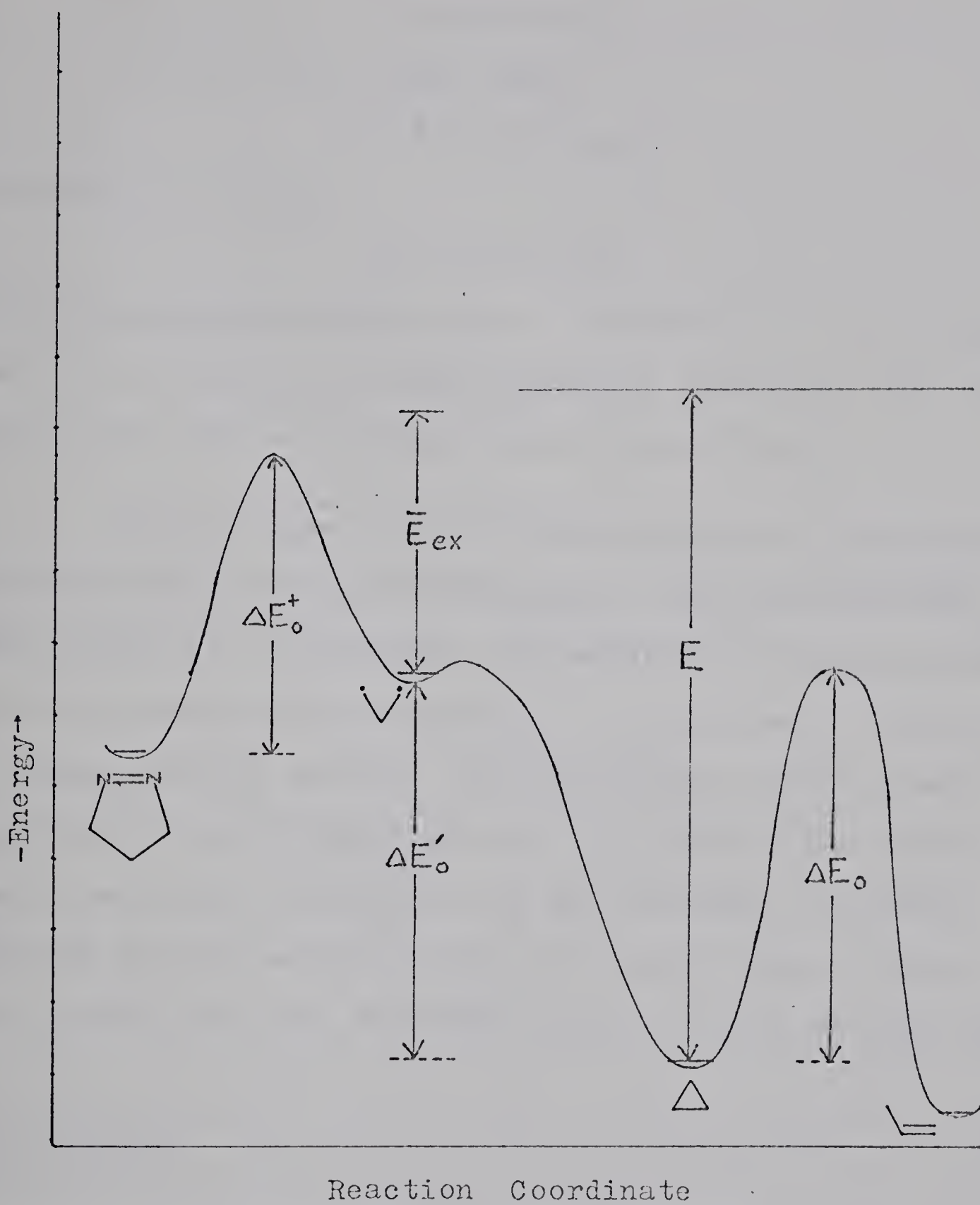


FIGURE 1

which yields,

$$E = 88 \text{ kcal/mole.}$$

With 600 mm of nitrogen added,

$$\beta = 2.47 \times 10^9 \text{ sec.}^{-1}$$

And solving for E we get,

$$E = 94 \text{ kcal/mole}$$

The discrepancy between the two values is possibly due to the decreased deactivation efficiency of nitrogen compared to 1-pyrazoline. (The calculations assume 'hard' or completely deactivating collisions)

Roquitte found a value of $E = 86 \text{ kcal/mole.}$ for the cyclopropane formed from tetrahydrofuran (THF) photolysis. Setser and Rabinovitch found a value of $E \approx 111 \text{ kcal/mole.}$ for thermal and photochemical (4358 \AA) addition of methylene (from diazomethane) to ethylene and $E \approx 104 \text{ kcal/mole}$ for ketene photolysis at 3100 \AA . From the pressures needed to quench isomerization in the THF photolysis and in the methylene plus ethylene reaction we see that the value for E in our case should lie somewhere between 86 kcal/mole and 104 kcal/mole and probably nearer the former value, so the value of $E \approx 90 \text{ kcal/mole}$ appears to be of the right order.

(B) Discussion

(a) Energy Content of the Initially Formed Cyclopropane in the Photolysis of 1-Pyrazoline.

To attach an actual meaning to the energy values obtained in the preceding section we consider an energy profile diagram, Figure 1.

The value of E has been calculated to be 90 kcal/mole. At 25° the thermal energy^{13f} of cyclopropane is around 2 kcal/mole so that we now have,

$$\Delta E'_0 + \bar{E}_{ex} = 88 \text{ kcal/mole}$$

To determine the value of $\Delta E'_0$, we must choose a value for $\Delta H_f^0(\text{CH}_2)_3$. Benson^{6a} has calculated a value of 67 kcal/mole for $\Delta H_f^0(\text{CH}_2)_3$ based on a species which is a true diradical (pair of spectroscopic doublets). This value will be used initially, hence,

$$\begin{aligned} \Delta E'_0 &= \Delta H_f^0(\text{CH}_2)_3 - \Delta H_f^0(\Delta) \\ &= 67 - 13 \\ &= 54 \text{ kcal/mole} \end{aligned}$$

We now calculate \bar{E}_{ex} , which should be the amount of the total excess light energy retained by the C_3 fragment after photolysis.

$$\begin{aligned} \bar{E}_{ex} &= 88 - 54 \\ &= 34 \text{ kcal/mole} \end{aligned}$$

The total excess light energy in this case would be given by,

$$\begin{aligned} \Delta H_f^0(\text{Cyclopropane}) + h\nu - \Delta H_f^0(\text{CH}_2)_3 \\ &= 54 + 90 - 67 \\ &= 77 \text{ kcal/mole} \end{aligned}$$

The estimation of the heat of formation of 1-pyrazoline is made by using the value for cyclopentene (8.5 kcal/mole) and adding an appropriate value for substituting -N=N- for -CH=CH-. The heat of formation of azomethane is +43.2 kcal/mole³⁸ and of trans-2-butene, -2.18; we should thus have to add 45.4 kcal/mole on going from cyclopentene to 1-pyrazoline. Thus, 45.4 + 8.5 = 54 kcal/mole. This value assumes that the difference between the heat of formation of cis-azomethane and the heat of formation of trans-azomethane is comparable to the difference between the heat of formation

of cis-2-butene and the heat of formation of trans-2-butene.

The value of 77 kcal/mole for the total excess light energy in 1-pyrazoline photolysis results in a value of 0.44 for the fraction of excess light energy retained by the C_3 fragment ($\bar{E}_{ex}/77$). This value seems to be absurdly low, which may reflect an error in the method, or incorrect values for $\Delta H_f^0(\text{C}_3\text{H}_3)$ and $\Delta H_f^0(\text{CH}_2)_3$. If we use the value calculated by Hoffmann³³ of 57 kcal/mole for the heat of formation of the trimethylene intermediate, we get a value for $\Delta E_0'$ of 44 kcal/mole, and a value for \bar{E}_{ex} of 44 kcal/mole. In addition, the value of the total excess light energy now becomes 87 kcal/mole. This makes the fraction of the excess light energy retained by the C_3 fragment ~ 0.5 which still seems rather low. However, the value of 57 kcal/mole appears to be an improvement over Benson's value of 67 kcal/mole.

If one were to drop $\Delta H_f^0(\text{CH}_2)_3$ by another 10 kcal and lower $\Delta H_f^0(\text{C}_3\text{H}_3)$ by 10 kcal, then the fraction of excess light energy retained by the C_3 fragment would be 0.62, which is nearing a reasonable value.

(b) Cyclopropane Forming Reactions.

The cyclopropanes formed from the photolysis of the unsubstituted (1) and the monosubstituted (2 and 3) pyrazolines reveal very little about the nature of the intermediate, since it is not possible in these cases to have stereoisomers.

The yields of the cyclopropanes in the gas phase photolysis of 1-pyrazoline(1) and 3-methyl-1-pyrazoline(2) are somewhat lower than for the thermal process^{22a,c} which is expected, because of the

higher energy content of the initially formed products in the photolytic process. However, the yield of methylcyclopropane in the gas phase photolysis of 4-methyl-1-pyrazoline(3) is higher than in the thermal process (which gives a fifty-two percent yield of methylcyclopropane). The reason for the smaller percentage of cyclopropane in the thermal process as compared with the photochemical is not readily apparent.

The cyclopropanes formed in the photolysis of the disubstituted pyrazolines (4, 5, 6 and 7) reveal a little more information than the three previous examples.

A very curious feature arises from the photolysis of trans-(4), and cis-3,5-dimethyl-1-pyrazoline(5). It is seen that in the gas phase the trans compound exhibits stereoselectivity in a similar manner to the thermal decomposition while the cis exhibits the opposite behavior. In liquid phase the trans now exhibits behavior opposite to the thermal results while the cis shows stereoselectivity similar to the thermal decomposition. In general though, the stereoselectivity observed in the thermal process seems to be decreased in the photolytic process and conrotation does not appear to be the predominating path for the ring closure of the intermediate as it is in the thermal process. One should be cautious here though, because the thermal process would be expected to produce the lowest electronic singlet of the intermediate while the photolysis may produce a higher singlet. Hoffmann only predicts conrotatory ring closure for the lowest singlet since it is believed that the antisymmetric state is more stable than the symmetric one. Electronic states other than the lowest lying singlet may well prefer a disrotatory

ring closure or neither.

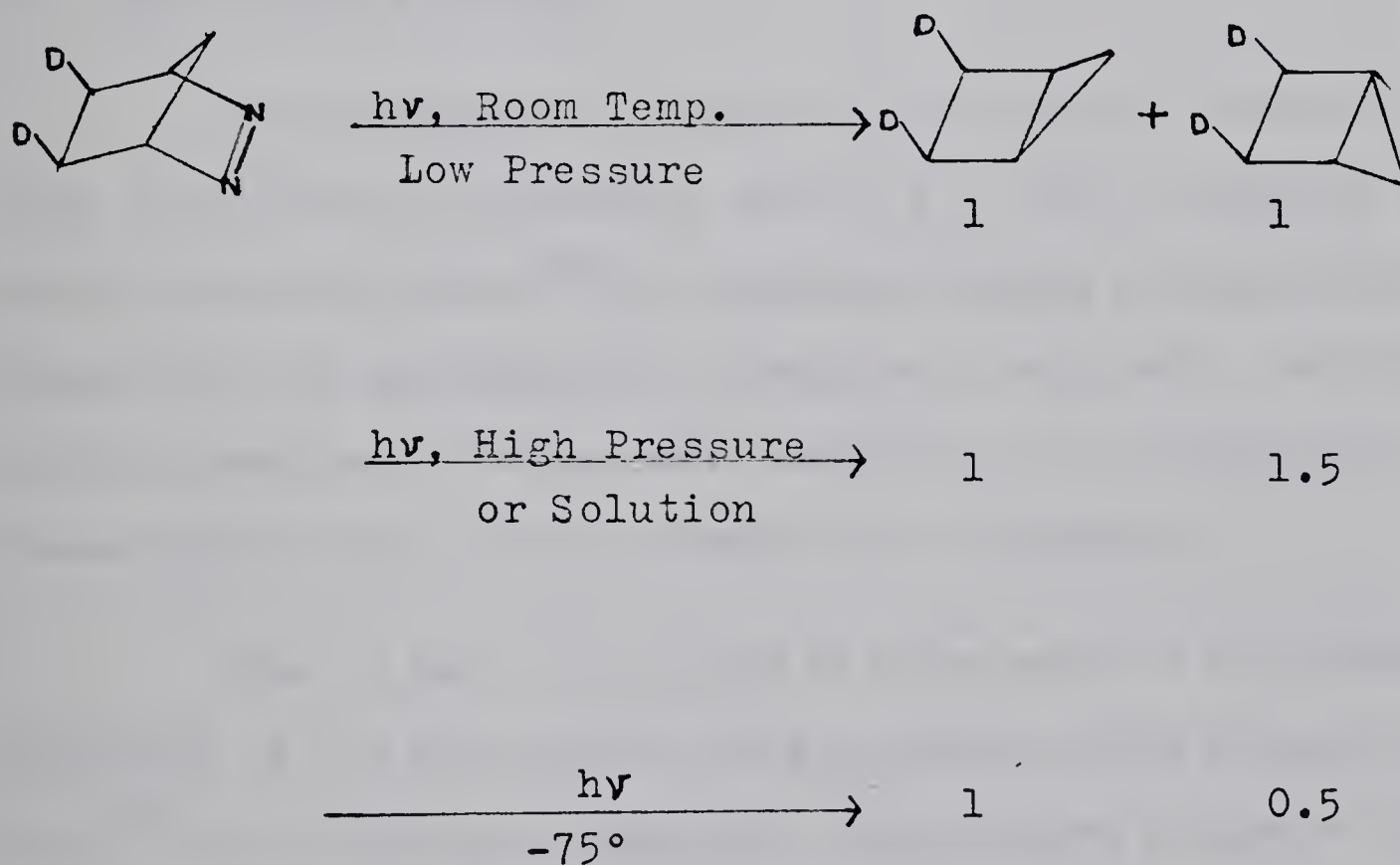
One may also be tempted to suggest here that since the true ground state of trimethylene intermediate has been predicted³⁴ to be a triplet, then in solution, some intersystem crossing may occur to give a triplet diradical which is expected to result in an increase in the amount of trans-DMCP. However, this is not supported by the results from the liquid phase photolysis of 6 and 7 (Tables 19 and 21).

In the direct photolysis results for trans-(6) and cis-3,4-dimethyl-1-pyrazoline(7) the cyclopropanes from both pyrazolines tend to retain the stereochemistry of the starting material. On increasing the pressure the cyclopropane forming reaction becomes even more stereoselective. Again, in this case, we have one compound 7 roughly paralleling the thermal results, while the other, 6, exhibits the opposite behavior. This again points out the differences between the ground state singlet and the excited singlet of the trimethylene intermediate. The cyclopropane ratios in this case tell even less than those from 4 and 5 because even if one could predict which rotation (con or dis) should predominate in ring closure, both rotations may give rise to either cis- or trans-DMCP.

The cyclopropanes formed do, however, follow the stereochemical

pattern found by VanAuken and Rinehart²³. They found that in the photolysis of cis- and trans-3,4-dimethyl-3-carbomethoxy-1-pyrazoline the resulting cyclopropanes tended to favor the stereochemistry of the substrate while the stereoselectivity was much less pronounced in the thermal results. This parallels fairly well the results for 6 and 7.

A peculiar result arises from the photolysis of 7 at 77°K. There is a reversal of stereochemistry of the cyclopropane products from the results at room temperature. This type of reversal has been observed previously by Roth and Martin³⁵, in the following:



The photosensitized decomposition of both 6 and 7 give rise to nearly the same cyclopropane ratios. The ratios are also fairly close to those obtained from 4 and 5 and may reflect a triplet intermediate which is free to rotate internally and longer lived than the singlet intermediate

which is presumably produced in the direct photolysis.

That the triplet diradical may be fairly long lived is in contrast to the conclusion of Kopecky et al.^{19a,b} who stated that spin inversion and ring closure must be fast in the case of the addition of triplet methylene to 2-butene because cis- and trans-2-butene did not produce the same product mixture. This conclusion was based on cis-2-butene giving two parts cis-DMCP and one part trans-DMCP, while trans-2-butene gave trans-DMCP as the major product with a very small amount of cis-DMCP and a trace of olefin.

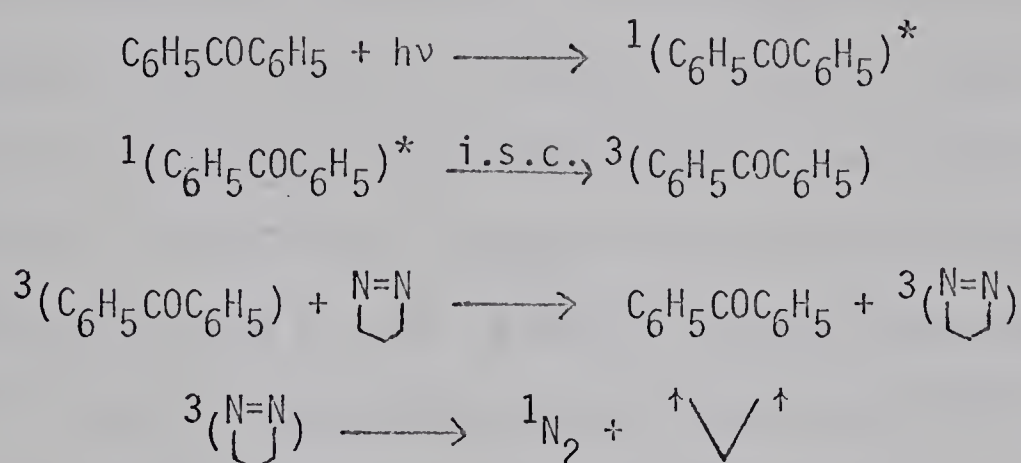
(c) Olefin Forming Reactions.

The photolysis of 1-pyrazoline(1) in solution (Table 11), produces a propylene to cyclopropane ratio of 1:9. This is identical with the result obtained by Mishra^{22d} for the thermal process and would lead one to suspect that the same mechanism is operating in each case. The higher yield of propylene in the gas phase photolysis of 1 is probably due to the isomerization of the initially formed 'hot' cyclopropane.

The 1:9 ratio of propylene to cyclopropane in the solution photolysis of 1 is not very near the high pressure value obtained by Klemm et al.³² for cyclobutanone photolysis. They obtained a value of 1:30 for 3130 Å light. Roquette²⁹ obtained a value of ca. 1:2.6 for THF photolysis. It is therefore quite possible in these two cases that the cyclopropane and propylene (at least not all) do not arise from the trimethylene diradical.

It is interesting that the photosensitized 1-pyrazoline which supposedly produces a triplet diradical (Scheme XIX) gives the same ratio of propylene to cyclopropane, 1:9. This is not altogether unexpected, because before ring closure may occur, there has to be spin inversion to the singlet.

SCHEME XIX



The 90:10 ratio of cyclopropane to propylene in the solution photolysis of 1 seems in accord with Benson's prediction⁵ that ring closure will be about ten times faster than hydrogen atom migration in trimethylene. It is also quite close to the value of 12:1 which was the ratio of cis - trans isomerization to propylene formation found for cis- and trans-cyclopropane-d₂¹⁹.

Benson has argued⁵ that the addition of singlet methylene to ethylene proceeds via a short lived diradical and indeed, at high pressures the value of the cyclopropane to propylene ratio has been found to be 85:15 for this reaction. However, there is no way to tell if the propylene arises from the direct insertion of methylene into C-H bonds or from the rearrangement of a trimethylene diradical. The similarity of the 85:15

ratio to the 90:10 ratio obtained for 1 may be fortuitous.

The olefin yields for the photolysis of 3-methyl-1-pyrazoline(2) are quite in line with the thermal results of Mishra^{22d} and Erikson^{22c}. The difference that does exist may be accounted for by the fact that 600 mm of nitrogen is not sufficient to completely quench the methylcyclopropane isomerization as evidenced by the presence of small amounts of isobutylene. We notice that olefin distribution is 1-butene > cis-2-butene > trans-2-butene. This is the same order observed in methylcyclopropane isomerization, addition of methylene to cyclopropane and in the thermal decomposition of 2^{22c,d}, (See Table 22). The ratio cis- + trans-2-butene/1-butene has a value of 1.1 at low pressures and ca.0.97 at 600 mm. These figures are practically identical to those for methylcyclopropane isomerization^{11,12}. On this basis it appears that cyclopropane isomerization goes through a trimethylene intermediate, the central hydrogen atoms of which show very little preference for migrating to either the primary radical end or the secondary radical end (Scheme XX).

SCHEME XX

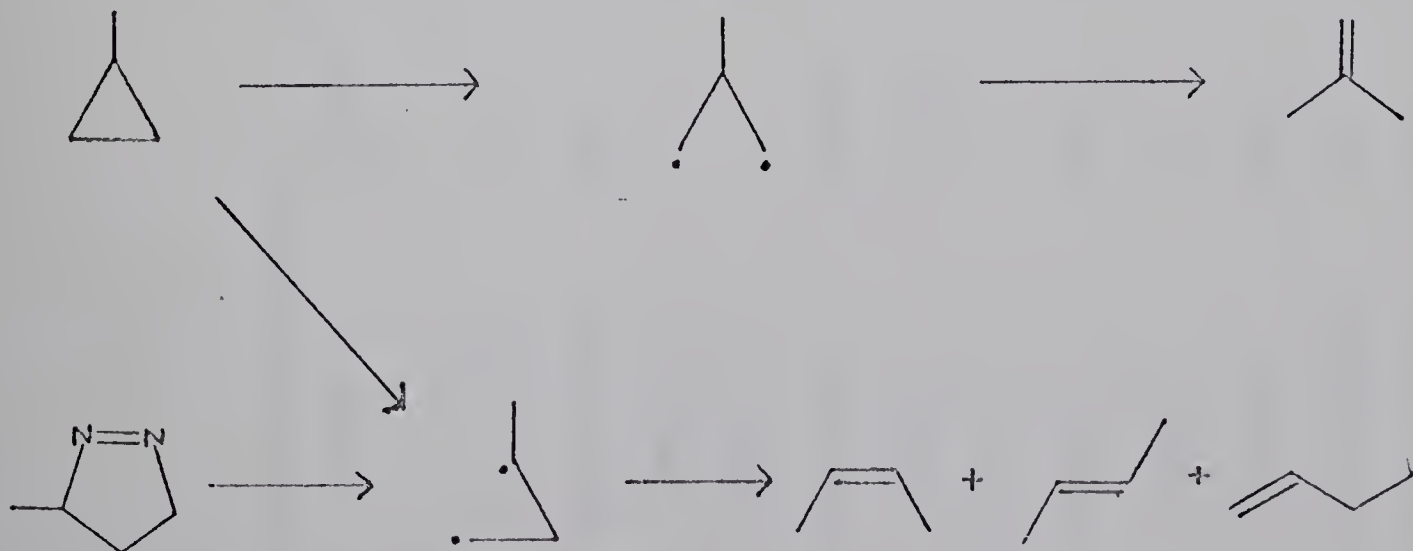


TABLE 22
RELATIVE BUTENE YIELDS FROM VARIOUS SOURCES

Source	Pressure Torr.	T, °C.	1-Butene	c-2-Butene	t-2-Butene	Isobutylene	Ref.
$\text{CH}_2^+ \Delta(h\nu)$	65.8	25	1.00	0.67	0.51	0.32	3
$\text{CH}_2^+ \Delta(h\nu)$	440	25	1.00	0.50 ₅	0.29	0.22	3
Therm. Δ	-	400	1.00	0.72	0.30	0.18	12
Therm. Δ	-	469	1.00	0.64 ₅	0.30	0.15	11
Therm. <u>2</u>	100-200	250	1.00	0.53	0.35	0	22a
Therm. <u>2</u>	100-200	218	1.00	0.63	0.34	0	22c
Phot. <u>2</u>	7-8	25	1.00	~ 0.85	0.22	-	Self
Phot. <u>2</u>	600(N_2)	25	1.00	0.90	~ 0.075	-	Self
Phot. <u>3</u>	7-8	25	1.00	0.67	0.48	-	Self
Phot. <u>3</u>	600(N_2)	25	1.00	0.8	0.14	-	Self
$\text{CH}_2 + \text{C}_3\text{H}_6(h\nu)$	101	25	1.00	0.33	0.26	0.23	3
$\text{CH}_2 + \text{C}_3\text{H}_6(h\nu)$	1970	25	1.00	0.23	0.21	0.20	3

It is difficult to see why the cis-2-butene should be so favored over the trans-2-butene. It suggests that the favored conformation of the diradical is that shown in Figure 2.

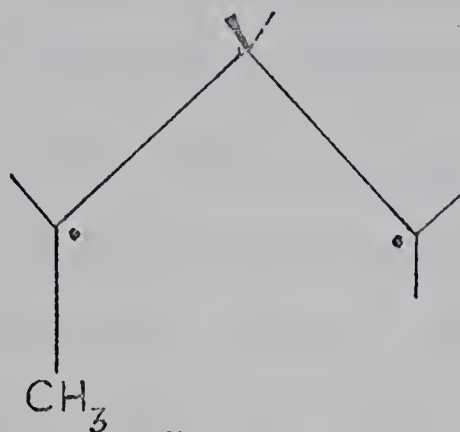


FIGURE 2

This cis configuration is not necessarily the least thermodynamically stable. Other compounds such as 1-bromopropylene favor a cis configuration and the mistake should not be made that the cis configuration of this trimethylene diradical is necessarily the least favored one.

The olefins, other than isobutene, in the photolysis of 4-methyl-1-pyrazoline(3) must come from the isomerization of a 'hot' methylcyclopropane. If such is the case, then it would be expected to find (cis + trans-2-butene)/1-butene about equal to 1, the value found for methylcyclopropane isomerization in other work. Such is indeed the case, for both the high pressure and low pressure regions. Also, the amount of olefin (isobutylene) formed from 3 is greater than the amount (cis + trans-2-butene + 1-butene) formed from 2. This might lead one to suspect that one of the main governing factors for hydrogen migration is not the center to which it migrates, but the kind of center it leaves. In the case of 2, the hydrogen departs from a secondary center and in 3, it departs from a tertiary center. It appears then that a hydrogen is more easily removed

from a tertiary center than a secondary one, which is the expected behavior for a radical type reaction.

Comparing the results from Table 12 (Page 50) to those obtained from the reaction of methylene with propylene does not yield much information as to the mechanism of the latter reaction. This is because all the olefins formed from 2 and 3 arise in the methylene reaction from direct insertion into various C-H bonds. Table 22 compares the relative butene yields from various sources. (In effect Table 22 is just Table 4 with the data from Table 12 added) Except for methylene addition to propylene, all of the ratios for the linear butenes are similar enough to lead one to suspect that they are arising from the same (or very similar) intermediate in each case. There is not much choice for this intermediate other than the substituted trimethylene diradical, (Figure 2).

One interesting fact about the methylene and propylene reaction at high substrate pressures may be mentioned, and that is if all the olefin is assumed to come from direct insertion^{3a,b}, and one applies the relative rates for methylene insertion into various C-H bonds, as determined by Butler and Kistiakowsky^{3a,b}, then the yields of cis- and trans-2-butene and isobutylene all approach the same value while the 1-butene yield works out to about three times this value. Making a statistical correction (dividing its yield by three) for the 1-butene yield results in all butenes having approximately the same yields. On the other hand, at lower pressures, where a considerable amount of isomerization of 'hot' methylcyclopropane would be expected to take place, the yields of the butenes tend to look similar to the results for the thermolysis of 2,

or the isomerization of methylcyclopropane (See Table 22, Page 72). The consequence of this is that the addition of methylene (singlet) to propylene does not appear to proceed through a trimethylene intermediate, while the isomerization of methylcyclopropane does seem to do so.

From the results of the direct photolysis of trans-(4) and cis-3,5-dimethylpyrazoline(5) in Tables 13 to 16 (Pages 51 to 54) it is immediately seen that the olefin (except cleavage products and branched pentenes) yields in the case of 4 are similar to the thermal process, while the olefin yields from 5 are quite different from the thermal process. The branched pentenes probably result from the isomerization of 'hot' dimethylcyclopropane, which appears to be completely quenched even on the addition of very small amounts (60 mm) of nitrogen gas. This is in contrast to the case of 1-pyrazoline where even 600 mm of nitrogen gas does not completely quench the cyclopropane isomerization. This may be explained by the fact that the DMCP has many more vibrational degrees of freedom than cyclopropane and hence, a 'hot' molecule will have less tendency to isomerize.

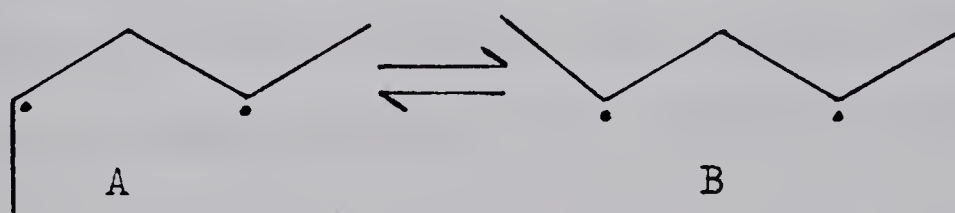
The addition of large excesses of nitrogen appeared to have little effect on the product distribution except maybe to make the cyclopropane forming reaction a little more stereoselective, but it is doubtful if any significance can be attached to this because the change was so small. The fact that something unusual is occurring may be determined from the olefin yields. Both cis- and trans-2-pentene appear in all direct photolyses products at room temperature which is to be contrasted with the thermal results where 5 does not give rise to any cis-2-pentene at all.

In the photolysis process the olefin yields parallel the thermal

results only at 77°K in an ethanol glass. At this temperature it was found that 4 gave equal amounts of cis- and trans-2-pentene, while 5 gave no cis-2-pentene at all (the trace observed probably due to the 15% of 4 present in 5). This is identical to the thermal result for olefin formation.

The olefin yields in the direct photolysis of 4 and 5 at room temperature seem to lend support to Hoffmann's prediction³³ that the excited singlet of trimethylene is a 'floppy' molecule. In the liquid phase (equivalent to infinite pressure) one would not expect any olefin formed to undergo geometrical isomerization, hence it appears as if from both trans-(4) and cis-3,5-dimethyl-1-pyrazoline(5) we get a mixture of diradical A and diradical B (Scheme XXI); that is to say, the diradicals A and B are interconvertible (rapidly equilibrating).

SCHEME XXI



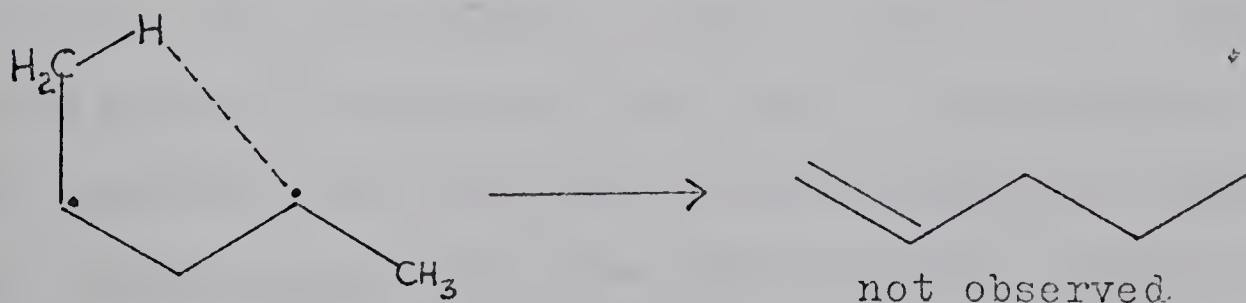
This is in contrast to the thermal results (where the singlet of trimethylene is produced) where the olefin yields (cis- and trans-2-pentene produced from 4 and only trans-2-pentene from 5) dictate fixed, non-equilibrating intermediates. This is in accord with Hoffmann's calculations which predict the singlet to have a fairly large energy

barrier to internal rotation, while in the excited singlet there is a very small barrier to rotation.

It is interesting to note that the photosensitized decomposition of both 4 and 5 decrease the olefin yield to near zero and it may be that the small amounts seen are due to some direct photolysis taking place. Alternatively, it is practically inconceivable that the triplet diradical could produce olefins directly, so after spin inversion occurs, the resulting intermediate is probably completely collisionally stabilized and may close almost exclusively to the cyclopropanes. It has been shown in the thermal isomerization of dimethylcyclopropanes that cis-trans isomerization occurs 100 times faster than olefin formation^{6b,10}, so the collisionally deactivated intermediate would be expected to give no more than a total of around one percent olefin.

The photosensitized results for 4 and 5 show no trace of 1-pentene. This product would be expected to arise if the triplet diradical underwent a 1,4-hydrogen migration (Scheme XXII) similar to that proposed^{13k} for the formation of 3-methyl-1-butene in the addition of triplet methylene to 2-butene.

SCHEME XXII



The interesting products from the photolysis of trans-(6) and cis-3,4-dimethyl-1-pyrazoline(7) are the olefins, and in particular, the 2-methyl-1-butene (Tables 18 to 21). In the case of singlet methylene addition to 2-butene, there is no way for 2-methyl-1-butene to be formed by direct insertion into a C-H bond, whereas for 6 and 7 both the thermolysis^{22b} and the direct photolysis give rise to substantial amounts of this product. In the addition of singlet methylene to 2-butene, the olefin 2-methyl-1-butene is seen only at low pressures where the isomerization of the initially formed cyclopropanes is not completely quenched. However, the trimethylene intermediate produced from 6 and 7 always yields this product even under very 'cool' conditions (77°K). This then appears to eliminate the possibility of singlet methylene initially giving rise to a trimethylene intermediate when it adds to olefins, no matter how short lived that intermediate is. This is directly opposed to the suggestion of Benson⁵ and is in accord with the predictions of Hoffmann³³, the experimental observations of Ali^{22b}, and the idea of Skell and Woodworth put forward in 1956^{13b}.

The data from the photosensitized decomposition of 6 and 7 again shows a large decrease in the olefin yield. This, coupled with the results from 4 and 5, leads one to the conclusion that the triplet diradical probably produces only trace amounts of olefin, if any at all. The results of Bader and Generosa^{13k} support this idea since at high pressures of inert gas (where supposedly the concentration of triplet methylene is high) when methylene is added to cis-2-butene, the yield of 2-methyl-1-butene is zero and the 2-methyl-2-butene is tending to zero. The small amount of 2-methyl-2-butene present may result from singlet insertion or from some abstraction

recombination mechanism involving triplet methylene, (See Scheme VIII).

Neither cis- nor trans-3,4-dimethyl-1-pyrazoline gives rise to any 3-methyl-1-butene in either direct or photosensitized photolysis. It follows then that no 1,4-hydrogen migration is taking place. It therefore appears very unlikely in the case of triplet methylene addition to 2-butene that the 3-methyl-1-butene is arising from a 1,4-hydrogen migration, unless the activation energy for such a process is quite high and not attained in the case of 6 and 7. However, as mentioned before, it is difficult to see how a 1,4-migration can take place without accompanying 1,2-migration. It therefore appears more likely that the 3-methyl-1-butene arises from some type of abstraction recombination mechanism as in Scheme VIII.

Another interesting feature of the decomposition of 6 and 7 is the total C₅ olefin yield. The trans-isomer, 6, has about thirty percent of its product comprised of olefin, whereas for the cis-isomer, 7, only seven to nine percent olefin is produced. Ali^{22b} has shown that, in the thermolysis of 6 and 7, isomeric intermediates are produced (Schemes XIV and XV), and that the cis-pyrazoline 7 gives rise to less olefin than the trans-pyrazoline 6. This difference, however, is more pronounced in the photolysis process. It would therefore seem that intermediate IV (Figure 3) from 6 is more favorable for olefin formation than intermediate III from 7.



FIGURE 3

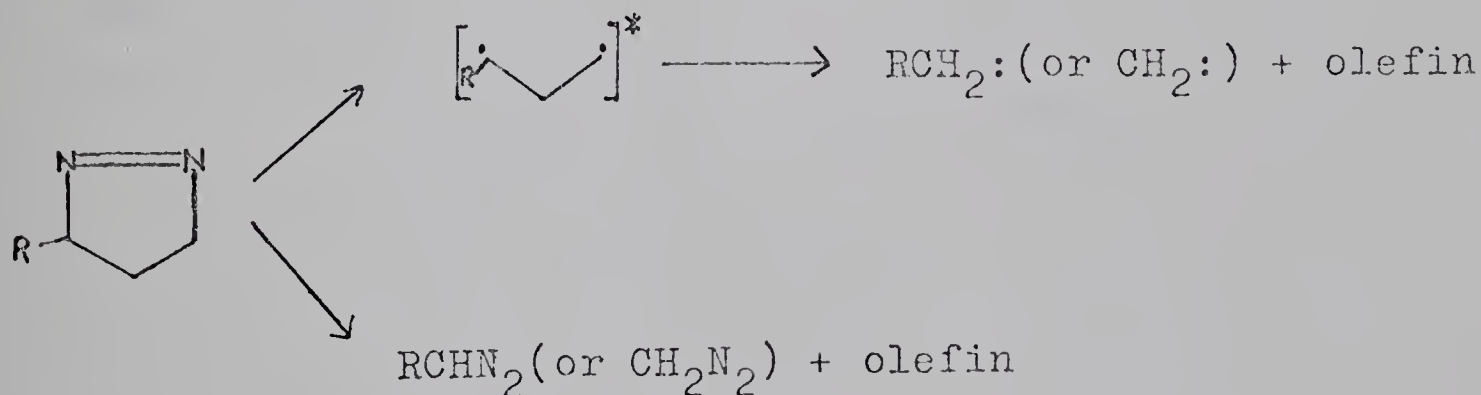
The reason for this is not readily apparent.

(d) Cleavage Reactions.

Carbon-carbon bond cleavage products have been observed in the photolysis of 1-pyrazolines before^{23,26}. One instance of cleavage has also been observed by Mishra^{22d}, in the thermolysis of 4,4-dimethyl-1-pyrazoline. In all direct photolysis of the pyrazolines investigated in this work cleavage products were observed.

Two routes are possible for the formation of cleavage products (Scheme XXIII):

SCHEME XXIII



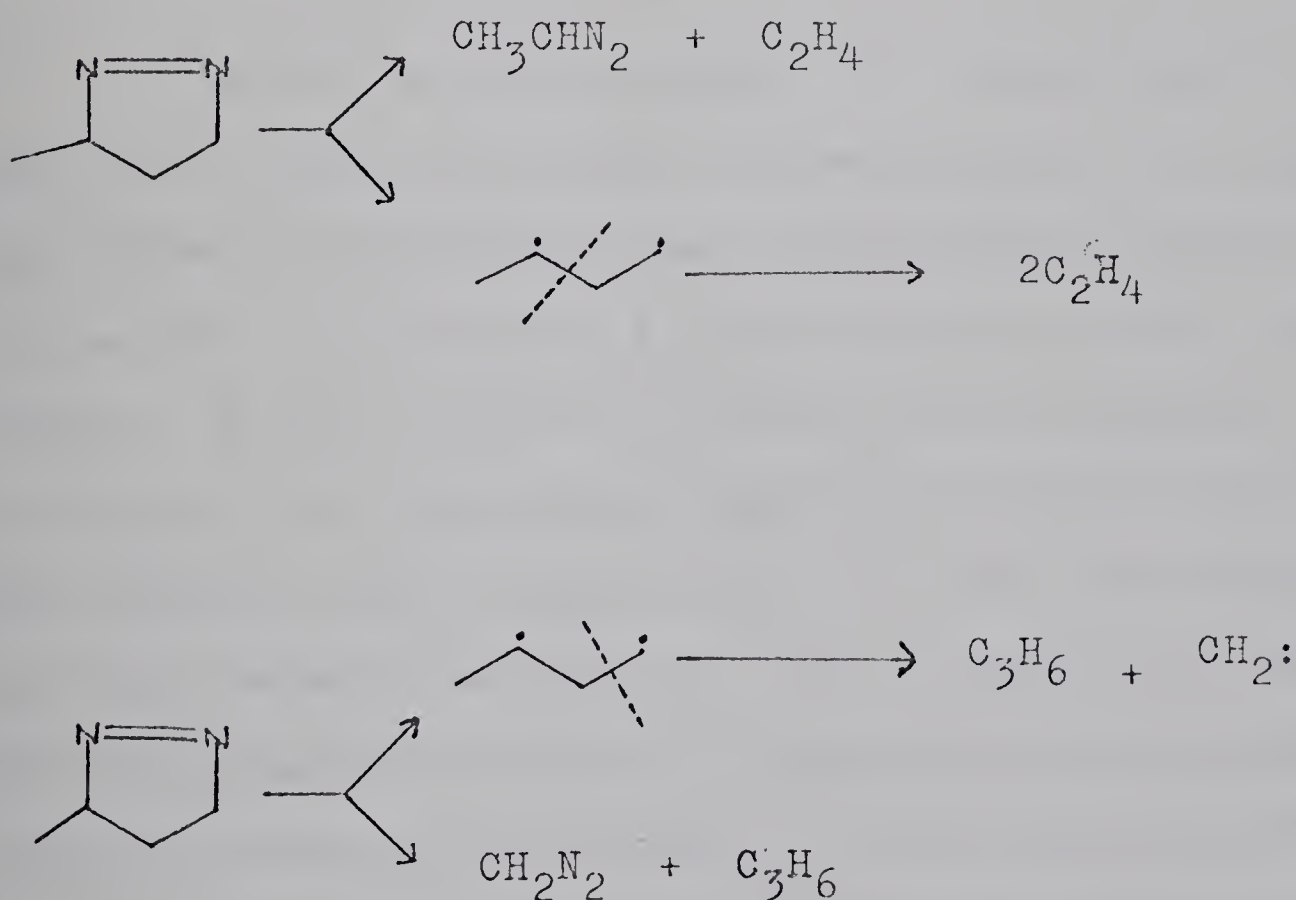
Both paths 1 and 2 would eventually lead to the production of either methylene, for pyrazolines unsubstituted in the 3-position, or ethylidene, for pyrazolines with a methyl group in the 3-position.

That methylene is produced from the photolysis of 1-pyrazoline(1) is virtually proven by the presence of 1,1,2,2-tetramethylcyclopropane resulting from the photolysis of 1 in 2,3-dimethyl-2-butene solvent. In

addition to this, all direct photolyses carried out in ethanol produced small amounts of either methyl ethyl ether or diethyl ether. These other products quite probably arise from the reaction of methylene or ethylidene with the O-H bond of the alcohol solvent.

The photolysis of 3-methyl-1-pyrazoline(2) results in two different cleavage products. These arise from the cleavage of two different carbon-carbon bonds, (Scheme XXIV):

SCHEME XXIV



The route resulting in propylene formation is the preferred one according to the results, and it appears to be essentially pressure independent.

The other mode of cleavage is also likely pressure independent.

In the photolysis of 4-methyl-1-pyrazoline(3) only one cleavage product is possible, propylene. This was the only cleavage product observed.

No matter by which route cleavage occurs (Path 1 or 2, Scheme XXIII), both trans-(4) and cis-3,5-dimethyl-1-pyrazoline(5) can only produce two olefins, ethylene and propylene. These olefins were observed in six to nine percent yield in the direct photolysis runs.

So far, the cleavage products tell nothing regarding the mechanism of their formation. However, the cleavage products from trans-(6) and cis-3,4dimethyl-1-pyrazoline(7) impart somewhat more information than the previous ones. The pyrazoline 6 yielded ethylene, propylene and only trans-2-butene. Not even a trace of cis-2-butene could be detected. The opposite is true for 7, only cis-2-butene (other than ethylene and propylene) was found and not a trace of trans-2-butene. This means that the cleavage reaction is entirely stereospecific. This is identical with the result obtained by VanAuken and Rinehart²³ in the photolysis of cis- and trans-3,4-dimethyl-3-carbomethoxy-1-pyrazoline. It is very hard to conceive of a diradical which fragments before it undergoes some internal rotation. If the cleavage products were arising from the diradical (Path 2, Scheme XXIII), then we should expect to see both cis- and trans-2-butene from 6 and 7. However, because of the stereospecificity, the favored route is Path 1,

(Scheme XXIII), which supports the mechanism of VanAuken and Rinehart²³. If Path 1 is operative, then this is just the reverse of the 1,3-dipolar addition of diazomethane to olefins. However, the addition is a thermal process while the reverse is only observed photochemically. The reason for this is not at all clear at present.

SUMMARY

While very little may be concluded from the stereochemistry of the dimethylcyclopropanes in the photolysis of cis- and trans-3,5-dimethyl-1-pyrazoline, it appears that the diradical formed is much less stereoselective in its reactions than that produced thermally. This is in line with Hoffmann's prediction that the excited singlet and the triplet state of the trimethylene diradical should be 'floppy'; and that the lowest singlet, which is produced in thermolysis, is somewhat more rigid. The olefins in the case of the 3,5-dimethyl-1-pyrazoline also support this idea.

The olefins produced from 3,4-dimethyl-1-pyrazoline do not lend support to the idea that singlet methylene adds to olefins via a diradical mechanism but instead support a concerted process which gives cyclopropanes directly. In view of the yields of 2-methyl-1-butene obtained in this work and that of Ali, it is difficult to arrive at any other conclusion.

The conclusion of Bader and Generosa that 2-methyl-1-butene does not appear to be a product in the addition of triplet methylene to cis-2-butene is supported by the fact that very little or no olefin is produced when the triplet diradical is produced by benzophenone photosensitization. However, the proposed mechanism for the formation of 3-methyl-1-butene in triplet methylene addition to 2-butene cannot be supported by the present results. Its presence was not observed (not even trace amounts) in the photosensitized decomposition of 6 and 7. Neither was 1-pentene observed under similar conditions from either 4 or 5.

The pyrazolines studied here were found to lose the elements of

diazomethane or diazoethane in a photochemical process similar to that observed previously²³. The process was found to be completely stereospecific, which supports the idea of the cleavage products arising directly, in a concerted process, from the starting pyrazoline²³ and not from an intermediate diradical. Why the retro-1,3-dipolar addition should be a photochemical and not a thermal process is not obvious at present.

CHAPTER IV

EXPERIMENTAL

All ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Nuclear magnetic resonance spectra were obtained on Varian Associates A-60 and HR-100 spectrometers. Mass spectra were measured on an A.E.I. MS-9 mass spectrometer.

(A) MATERIALS

(a) The 1-pyrazolines.- All the pyrazolines used have been prepared previously. Pyrazolines 1, 2, 3, 4 and 5 were prepared in the manner described by Mishra^{22d} from the corresponding 1,3-dibromides. All were purified by preparative gc using an Aerograph Autoprep. Model A-700. Each pyrazoline was checked for purity by nmr. Pyrazoline 5 was found to contain 15% 4 by 100 mc nmr. Ultraviolet spectra of all pyrazolines were determined to ensure the absence of an appreciable amounts of 2-pyrazoline.

Pyrazolines 6 and 7 were prepared following the procedure of Ali^{22b} from the appropriate 2-butene and diazomethane. These were also purified by preparative gc., and checked for purity by nmr. and uv. spectra.

All of the pyrazolines were stored in break seals at -78°C. for indefinite periods with no detectable deterioration.

(b) Hydrocarbon Standards for Gas Chromatography.- All reference hydrocarbons, with the exception of 2,3-dimethyl-2-butene (TME), were

commercially available and used directly from cylinder or bottle, (Table 23).

2,3-Dimethyl-2-butene.- Methyl iodide (361 g, 2.55 moles) was slowly added to a vigorously stirred mixture of magnesium turnings (62 g, 2.55 moles) in 500 ml of dry ether. The addition rate was adjusted to allow gentle refluxing. After all the methyl iodide was added, a solution of 3-methyl-2-butanone (200 g, 2.3 moles) in 100 ml of dry ether was slowly added with vigorous stirring. Again the rate was adjusted to allow gentle reflux. Stirring was continued for 3 hrs. after the addition was complete.

A saturated solution of ammonium chloride was slowly added to the above mixture until no more heat was evolved. The ether layer was separated and the aqueous layer extracted twice with ether. The extracts were combined, and to the aqueous suspension of magnesium salts just enough dilute HCl was added to clear the solution. This was then extracted twice with ether. All ether extracts were combined and dried over anhydrous sodium carbonate. The solvent was removed by evaporation and the residue distilled at atmospheric pressure through a Vigreux column. All material boiling under 55° was discarded and the residue placed in a 3-necked flask equipped with magnetic stirrer, a 30 cm distilling column packed with glass helices, and heated to $110-120^{\circ}\text{C}$. A solution of 50% sulfuric acid in water was then added dropwise and the fraction distilling between 55 and 75° was collected. This fraction was then redistilled through a good column to produce 47.4 g (0.56 moles, 25% yield from starting ketone) of tetramethylethylene (TME). B.p. $65-69^{\circ}$.

The TME prepared this way had small amounts of 3-methyl-2-butanone

TABLE 23
REFERENCE HYDROCARBONS FOR GC

Hydrocarbon	Source	Grade	Purity, %
Ethylene	Phillips	Research	99.85
Propylene	Phillips	Research	99.78
Cyclopropane	Ohio		>99
1-Butene	Phillips	Research	99.69
<u>cis</u> -2-Butene	Matheson		95
<u>trans</u> -2-Butene	Matheson		95
Isobutylene	Phillips	Research	99.51
2-Methyl-1-butene	Phillips	Pure	>99
2-Methyl-2-butene	Phillips	Pure	>99
3-Methyl-1-butene	Phillips	Pure	>99
<u>cis</u> - and <u>trans</u> -2-Pentene	Phillips	Pure	>99
<u>cis</u> -DMCP	Am. Pet. Inst.	Cert.	99.77
<u>trans</u> -DMCP	Am. Pet. Inst.	Cert.	99.87
1,1,2,2-Tetramethyl- cyclopropane	Am. Pet. Inst.	Cert.	99.96

and 3-methyl-2-butanol present. However, when it was stored over lithium aluminum hydride for several days, these impurities were removed and the product was pure by gc. and nmr.

(B) APPARATUS

(a) Vacuum Rack. - A conventional high vacuum apparatus with a Welch Duo Seal vacuum pump and a mercury diffusion pump was used, (Figure 4). The system consisted of a 250 ml quartz cell, A, for gas phase photolysis; three standard U-traps, 1, 2, 3, along with a small U-trap, 4; a spiral trap, F; a $\frac{5}{20}$ ground glass joint, B; mercury float valves, G and H; and a system for the introduction of samples into the gc, E. Section E consisted of two, three-way Hoke valves bolted on the ends of a piece of wood, and a two-way Hoke valve bolted in the middle as shown. Point J represents where the effluent gas from the gc could be diverted into the apparatus for the collection of any desired fraction in trap F. Point C was used for break seals in which material trapped in F could be stored. Point D was used for break seals containing product from liquid photolysis in order to analyze the product in the gc.

The light source used was an Osram 200W super pressure mercury arc with a Corex glass filter.

(b) Gas Chromatography. - An F and M Model 500 programmed temperature gas chromatograph was used for product analysis of the photolysis of 1-pyrazoline(1) in TME.

All other product analyses were done on a gc consisting of a Gow-Mac Model TR-II-B, w thermal conductivity cell with a Gow-Mac Model

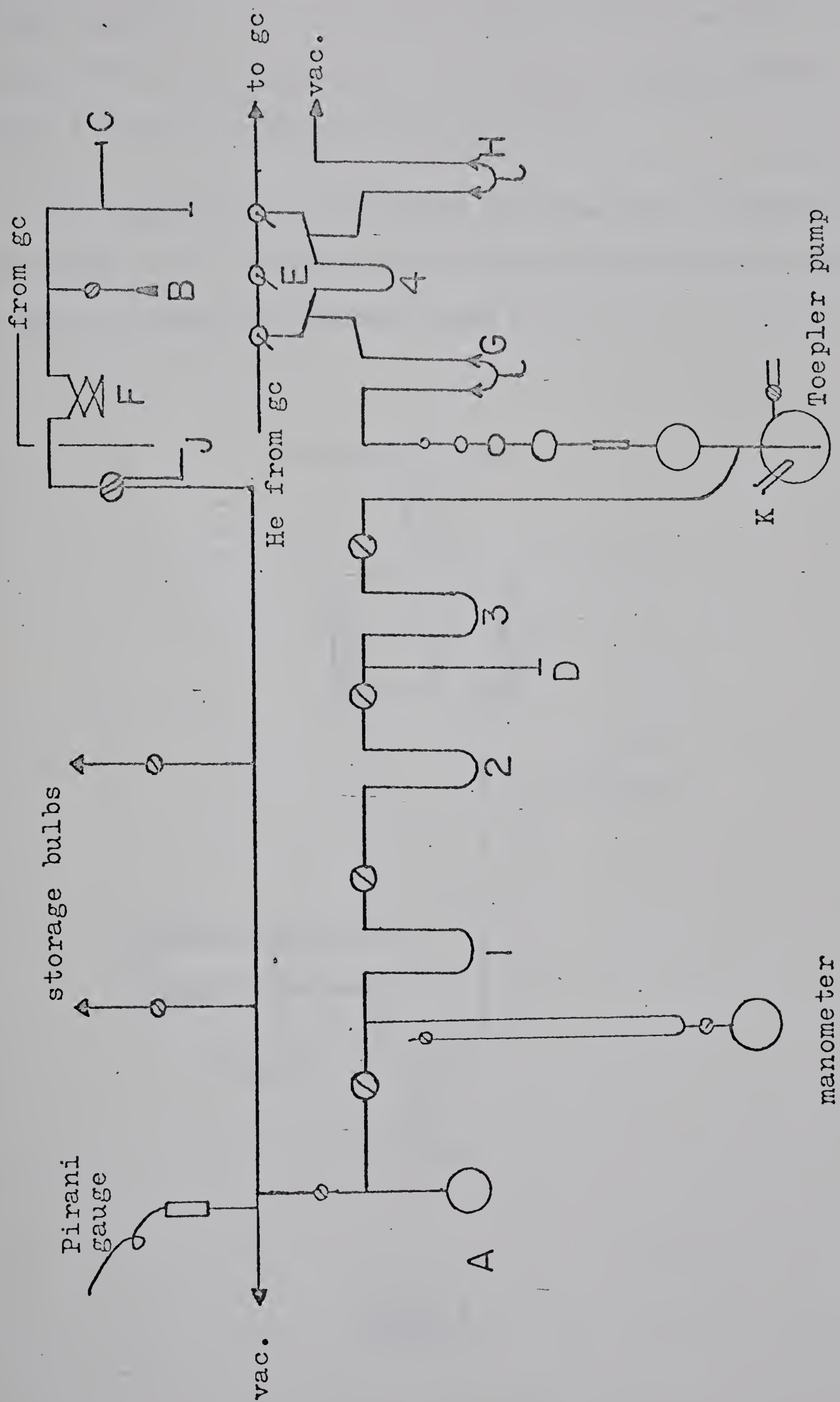


FIGURE 4

40-05C power supply in conjunction with a Sargent Model SR recorder. The helium used with this system was purified by passing through ascarite followed by a column of molecular sieves 4A at 77°K.

(c) Bulb Crusher.— Photolyses in ethanol were carried out in sealed glass bulbs which were crushed directly in the helium carrier gas flow by use of a heated bulb crusher, Figure 5.

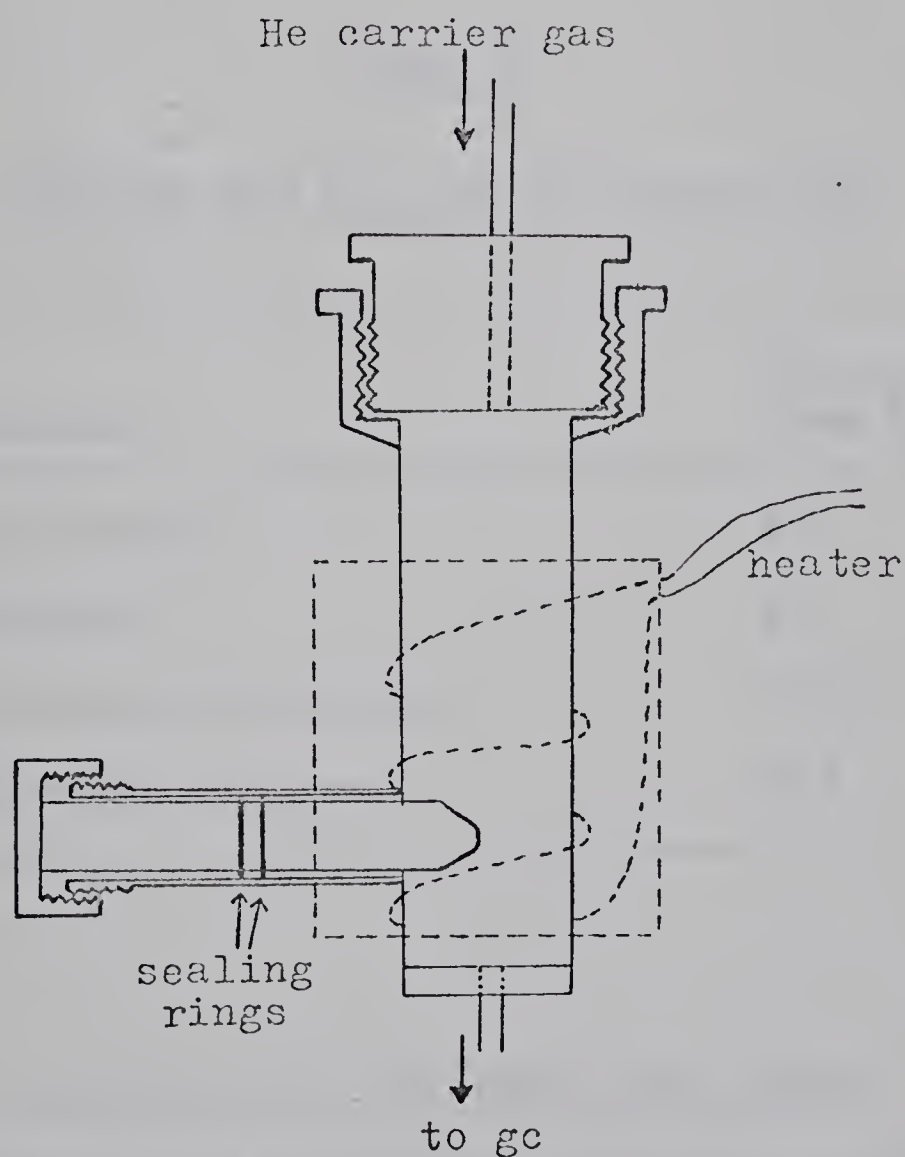


FIGURE 5

(c) PRODUCT ANALYSIS

(a) 1,1,2,2-Tetramethylcyclopropane, - For the analysis of 1 in TME a 20 ft column of saturated silver nitrate in propylene glycol on Diatoport was used in tandem with 20 ft of 10% 1,2,3-tris (2-cyanoethoxy)-propane (TCP) on firebrick. The columns were used at room temperature with a helium flow rate of 50 ml/min. The retention data for this system are given in Table 24.

TABLE 24

RETENTION DATA FOR AgNO₃-TCP COLUMN SYSTEM

Compound	Minutes from Air
Cyclopropane	1.0
Propylene	4.2
Tetramethylcyclopropane	9.2-9.5
Tetramethylethylene	12.7

(b) Products of All Photolyses Except Above. - The products from the photolysis of all pyrazolines in gas phase or ethanol were determined using a 20 ft column of saturated silver nitrate/propylene glycol on firebrick in tandem with a 9 ft column of 20% dimethylsulfolane (DMS) on Chromosorb W. The columns were used at room temperature with a flow rate of 60 ml/min helium. In some cases where serious overlapping of peaks

TABLE 25

RELATIVE RETENTION DATA FOR HYDROCARBONS

ON AgNO₃-DMS COLUMN

Hydrocarbon	Rel. Ret. Time (<u>trans</u> -DMCP=1.000)
(Air)	0.503
Ethylene	0.646
Propylene	0.822
Cyclopropane	0.710
<u>trans</u> -2-Butene	0.957
<u>cis</u> -2-Butene	1.446
Methylcyclopropane	0.810
Isobutylene	1.100
1-Butene	1.455
<u>trans</u> -DMCP	1.000
<u>cis</u> -DMCP	1.333
<u>trans</u> -2-Pentene	1.605
<u>cis</u> -2-Pentene	2.645
2-Methyl-2-butene	1.677
2-Methyl-1-butene	2.113
3-Methyl-1-butene	1.860
1-Pentene	2.210
(Diethyl ether)	2.330

occurred in this system, it was necessary to run the product mixture through either the silver nitrate or the DMS column separately in order to isolate a certain peak and determine its area relative to another peak (or peaks). The retention data for the silver nitrate-DMS column is given in Table 25.

Peak areas were measured by using a planimeter and all were corrected for relative responses^{36,37}.

(D) PHOTOLYSES PROCEDURE

The photolyses and product analyses of all compounds were performed in the same way (except 1 in TME and neat 4), so only typical representative cases will be given.

(a) Photolysis of 1 in TME.- To a 10 ml quartz cell, 1 cm thick, was added a solution of 0.245 g of 1-pyrazoline in 9.0 ml of TME. The solution was degassed by bubbling nitrogen gas and the cell attached to a mercury filled gas buret. After 15 hr irradiation, the solution was frozen using liquid nitrogen and allowed to remain frozen for 2 hrs. This would presumably freeze down most of the cyclopropane and propylene which left the solution. Following this it was found that 70% of the theoretical amount of nitrogen had been evolved. The solution was then allowed to come to room temperature and a sample was taken into a syringe for injection into the gc. The percentages of products found were; cyclopropane, 77%; propylene, 14%; and tetramethylcyclopropane, 8-9%. These values are practically meaningless quantitatively due to the almost certain loss of the low boiling products, propylene and cyclopropane. However, the purpose

of the experiment was accomplished by virtually proving the presence of methylene in the reaction as evidenced by the presence of tetramethylcyclopropane.

(b) Photolysis of 5 - Gas Phase with no Nitrogen added.- The pyrazoline 5, which was stored in the vacuum rack at -78°C , was allowed to come to room temperature. Its vapor pressure was found to be 5-6 mm as measured with the mercury manometer (Figure 4). The pyrazoline vapor was then allowed to flow into the reaction cell, A, and the cell isolated from the rest of the system. The residual pyrazoline vapor was then pumped off. The light source was allowed to warm up for approximately 15 minutes, then placed about 15 cm from the reaction cell and the sample irradiated for 60 minutes, after which time anywhere from 40-50 μmoles of pyrazoline was found to have decomposed.

After the lamp was turned off, traps 1 and 2 were cooled to 77°K , and the nitrogen pumped through them into the Toepler pump where it was measured. It was found necessary to use 30-35 cycles of the Toepler to remove the nitrogen. The nitrogen was then removed through float valves G and H. Following this, traps 1 and 2 were warmed to -78°C using dry ice-acetone baths and the hydrocarbon products distilled into the Toepler pump by means of the cold finger, K, at 77°K . This method was found to practically quantitatively distil over the hydrocarbons while the unreacted pyrazoline remained in traps 1 and 2. The hydrocarbons were measured in the Toepler and then frozen over into trap 4. Some typical values for the amounts of nitrogen and hydrocarbons are given in Table 17.

After isolating trap 4 with float valves G and H, the helium

carrier gas was diverted through the trap, after the trap had been allowed to warm to room temperature. The hydrocarbons were thus swept into the gc where they were analyzed. Any material which required further identification was collected by connecting the line from the gc to the vacuum system at point J and allowing the helium to flow through the spiral trap F, cooled to 77°K, and out through joint B. After removing the helium, the product could be transferred into a break seal at point C.

(c) Photolysis of 5 - Gas Phase with 600 mm Nitrogen Added.-

After the pyrazoline vapor had been introduced into and isolated in cell A, (as in previous example), it was frozen down with liquid nitrogen and the residual pyrazoline in the system pumped off. Nitrogen gas, which had previously been introduced into a storage bulb through a trap cooled in liquid nitrogen, was then allowed to flow into cell A until the desired pressure was attained. Cell A was then isolated and the pyrazoline frozen down in it allowed to come to room temperature, after which, the sample was irradiated for an appropriate period.

After irradiation was complete, traps 1, 2 and 3 were cooled to -77°K, and the nitrogen pumped off slowly. After all the nitrogen was removed (approximately 3 hours), the traps were warmed to -78°C, and the products treated exactly as in the previous example. It was found that the rate of photolysis with nitrogen added was comparable to that with no nitrogen present.

(d) Direct Photolysis of 5 in Ethanol.- A solution of 0.213 g of 5 in 5.00 ml of 95% ethanol was prepared. This results in 0.435 M solution, which was stored in a refrigerator at approximately -10°C. For

photolysis, 0.40 ml of this solution was diluted with 1.60 ml of 95% ethanol and the resulting solution used to fill several small pyrex glass bulbs (~0.3 ml). The bulbs were then thoroughly degassed (3-5 freeze-thaw cycles) on the vacuum line at point B (Figure 4) and sealed. A bulb containing the degassed solution was then irradiated for one hour at a distance of about 15 cm from the light source.

After irradiation, the bulb was placed in the bulb crusher (Figure 5) which was connected to the gc, heated to 110° and crushed. The hydrocarbon products were separated from the ethanol and unreacted pyrazoline by using a 20 ft column of 20% Carbowax 1500 on Chromosorb W. (This column separated the hydrocarbons from ethanol by more than 25 minutes and from the pyrazoline by an even larger amount). The column was used at room temperature with a flow rate of 40-50 ml/min. The hydrocarbon product was collected in trap F. After the helium was pumped off, the product was frozen into a break seal at point C, sealed and transferred to point D. The break seal was broken, the products frozen into the Toepler pump and measured. They were then transferred to U-trap 4, and passed into the gc which now has the silver nitrate-DMS column installed. The amounts of product typically found for 2 hours irradiation ranged from 15-25 μ moles.

(e) Benzophenone Photosensitized Photolysis of 5.- A solution of 1.59 M benzophenone (B.D.H. reagent grade, twice recrystallized) in 95% ethanol was prepared. This solution (1.60 ml) was then used to dilute 0.40 ml of the previously described solution of 5. This gave a solution which was 0.087 M in 5 and 1.27 M in benzophenone, a molar ratio of

benzophenone to 5 of 14.6:1. Since benzophenone and 5 have approximately the same molar extinction coefficient at 3200 Å, and benzophenone has a much broader absorption band, most of the incident light should be absorbed by the benzophenone. The solution was then put into bulbs, degassed, irradiated, and analyzed as described previously. Typical amounts of product for 2 hour irradiation were 8-13 μmoles.








(f) Photolysis of 4 Neat Liquid.- To a quartz epr tube fitted with an inner 5/20 joint was added liquid 5 to a height of about one-half inch. The tube was then attached at point D (Figure 4) through a stopcock by means of an outer 5/20 joint, degassed, and irradiated for two hours. After irradiation, the stopcock was opened and the liquid frozen over into U-trap 1. The nitrogen was then pumped into the Toepler and measured as previously described. Found, nitrogen, 23.2 μmoles. Traps 2 and 3 were then placed in dry ice-acetone baths (-78°C) and trap 1 allowed to warm to room temperature. The hydrocarbons were frozen over into the Toepler pump, measured, and found to equal 23.3 μmoles. The hydrocarbons were then passed into the gc and analyzed in the usual manner. The results have been given in Table 14.

(E) CONTROL EXPERIMENTS

(a) Product Lost on Trapping from GC.- A gas phase photolysis experiment was done on 5. The products were trapped and re-run through the gc as previously described. It was found that most of the ethylene was lost, about one-half of the propylene was lost, and the percent of other products almost unchanged. Actual results are given in Table 26.

TABLE 26

PRODUCT LOSS ON TRAPPING FROM GC

Compound	No. of Times Trapped	Product, mole%							
									C_2H_4
<u>5</u>	0	42.1	47.7	1.0	0.9	-	~0.15	-	8.2 7.6
	1	44.3	49.9	1.0 ₂	0.9 ₀	-	~0.14	-	3.7 1.5
<u>7</u>	0	37.8	43.2	0.87	0.57	4.37	4.72	7.15	1.28 0.92
	1	38.2	43.4	0.83	0.60	4.32	4.76	7.16	0.67 0.1 ₁

A similar experiment was also done on 7 and the results for this are also given in Table 26.

The results from 5 show that all C_5 hydrocarbons, if decreased, are decreased by the same amount. The results from 7 confirm this and in addition show that the C_4 hydrocarbon (cis-2-butene) is lost at the same rate as the C_5 hydrocarbons.

In addition to the above, several hydrocarbons were introduced into the system, measured in the Toepler, run through the gc, trapped, re-measured in the Toepler, run through the gc again, trapped, and measured again. The results for these are given in Table 27. The retention, in trap F, of the C_4 (trans-2-butene) is identical, within experimental error, with the retention of the C_5 hydrocarbons.

(b) Interconversion of DMCP under the Reaction Conditions.-

cis-1,2-Dimethylcyclopropane (56 mm) was placed in the reaction cell along with ~0.5 mm of 4, and irradiated for two hours. After irradiation, nitrogen found, 1.96 μ moles. Product analysis showed that the trans-DMCP peak was only 0.055% of the cis-DMCP peak and that the ratio of trans-DMCP to propylene equaled 3.04:1. In regular gas phase runs with 60 mm nitrogen present, the same ratio was 3.20:1 and 2.79:1. Since all the trans-DMCP may be accounted for by the decomposed pyrazoline and since the ratio of trans-DMCP to propylene is similar to that in regular gas phase runs, then it may be assumed that cis-DMCP is not converted to trans-DMCP under the reaction conditions. A similar result was obtained using trans-DMCP.

A small sample (37.7 μ moles) of cis-DMCP was added to a 1.27 M

TABLE 27

MATERIAL LOSS ON TRAPPING FROM GC^a

Compound	No. of Times Trapped	Amount, μ moles
Ethylene	original (0)	62.4
	1	10.1
	2	0.86
Propylene	original (0)	68.5
	1	39.6
	2	17.3
Cyclopropane	original (0)	61.9
	1	36.6
	2	21.0
<u>trans</u> -2-Butene	original (0)	56.9
	1	46.1
	2	38.9
<u>trans</u> -DMCP	original (0)	60.6
	1	49.7
	2	42.5
<u>cis</u> - and <u>trans</u> -2-Pentene	original (0)	53.3
	1	43.8
	2	37.8

^aHelium flow rate of 50 ml/min

benzophenone solution in ethanol in a small bulb, degassed and sealed. The solution was irradiated for three hours. The only detectable hydrocarbon after irradiation was cis-DMCP which measured 33.1 μ moles. Hence, cis-DMCP is not consumed or isomerized under reaction conditions.

(c) Undetected Products in Solution Photolysis.- A small pyrex glass bulb filled with the previously described solution of 5 in ethanol was attached at point D through a stopcock. After degassing, the stopcock was closed, and the solution irradiated for three hours. Following this, the stopcock was opened and the solution frozen over into U-trap 2. The nitrogen was pumped into the Toepler. The solution was then transferred into trap 1 and again the Toepler was used to remove any nitrogen. The nitrogen was measured and pumped off.

After the nitrogen was removed, the solution was frozen back into the pyrex bulb at D, and the bulb sealed off. It was then placed in the bulb crusher, run through the Carbowax column, and the products trapped in F as before, (Flow rate used in this case was 30-35 ml/min to minimize loss in trapping). The products were then transferred back to D and into the Toepler as before and measured.

Two similar experiments were carried out for the photosensitized decomposition of 5, except that now the DMS column was used in order to separate the acetaldehyde from the hydrocarbons.

The results for both these experiments are given in Table 28.

TABLE 28

DETERMINATION OF UNDETECTED PRODUCTS
IN SOLUTION PYRAZOLINE(5) PHOTOLYSIS

Photolysis Method	N ₂ μmoles	Hydrocarbons, μmoles	
		Theoretical ^a	Observed
Direct	21.33	22.4	18.8
Photosens	11.9	12.5	10.6
Photosens	9.64	10.12	8.44

^aAssuming that 5% of the reaction produces cleavage products.

Assuming that all the ethylene was lost and about 40% of the propylene was lost, the observed amounts of product corresponds to about 90% trapping efficiency which is a reasonable figure when compared to the measured losses in Table 27.

REFERENCES

1. (a) T. C. Chambers and G. B. Kistiakowsky, J. Am. Chem. Soc., 56, 399(1934)
(b) E. S. Corner and R. N. Pease, ibid., 67, 2067(1945)
(c) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, Proc. Roy. Soc. (London), A217, 563(1953)
(d) N. B. Slater, ibid., A218, 224(1953)
(e) R. H. Lindquist and G. K. Rollefson, J. Chem. Phys., 24, 725(1956)
(f) J. R. McNesby and A. S. Gordon, ibid., 25, 582(1956)
(g) B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, ibid., 28, 504(1958)
(h) E. W. Schlag and B. S. Rabinovitch, J. Am. Chem Soc., 82, 5996(1960)
(i) A. T. Blades, Can. J. Chem., 39, 1401(1961)
(j) B. S. Rabinovitch, D. W. Setser and F. W. Schneider, ibid., 39, 2609(1961)
2. C. E. H. Bawn and R. F. Hunter, Trans. Far. Soc., 34, 608(1938)
3. (a) J. N. Butler and G. B. Kistiakowsky, J. Am. Chem. Soc., 82, 759(1960)
(b) J. N. Butler and G. B. Kistiakowsky, ibid., 83, 1324(1961)
4. B. S. Rabinovitch, E. Tschuikow-Roux and E. W. Schlag, ibid., 81, 1081(1959)
5. W. B. DeMore and S. W. Benson, Adv. in Photochem., Vol. 2, 256(1964)
6. (a) S. W. Benson, J. Chem. Phys., 34, 521(1961)
(b) M. C. Flowers and H. M. Frey, Proc. Roy. Soc. (London), A257, 122(1960)
7. M. C. Flower and H. M. Frey, J. Chem. Soc., 2758(1960)
8. R. F. Klemm, D. N. Morrison, P. Gilderson and A. T. Blades, Can. J. Chem., 43, 1934(1965)

9. S. W. Benson and P. S. Nangia, J. Chem. Phys., 38, 18(1963)
10. M. C. Flowers and H. M. Frey, Proc. Roy. Soc. (London), A260, 424(1961)
11. J. P. Chesick, J. Am. Soc., 82, 3277(1960)
12. D. W. Setser and B. S. Rabinovitch, ibid., 86, 564(1964)
13. (a) G. B. Kistiakowsky and N. W. Rosenberg, ibid., 72, 321(1950)
(b) P. S. Skell and R. C. Woodworth, ibid., 78, 4496(1956)
(c) P. S. Skell and A. Y. Garner, ibid., 78, 5430(1956)
(d) R. C. Woodworth and P. S. Skell, ibid., 81, 3383(1959)
(e) H. M. Frey and G. B. Kistiakowsky, ibid., 79, 6373(1957)
(f) D. W. Setser and B. S. Rabinovitch, Can. J. Chem., 40, 1425(1962)
(g) H. M. Frey, Proc. Roy. Soc. (London), A251, 575(1959)
(h) H. M. Frey, J. Am. Chem. Soc., 80, 5005(1958)
(i) W. von E. Doering and P. LaFlamme, ibid., 78, 5447(1956)
(j) F. H. Dorer and B. S. Rabinovitch, J. Phys. Chem., 69, 1952(1965)
(k) R. F. W. Bader and J. I. Generosa, Can. J. Chem., 43, 1631(1965)
14. F. A. L. Anet, R. F. W. Blades and A. Van der Auwera, J. Chem. Soc., 82, 3217(1960)
15. (a) G. Herzberg and J. Shoosmith, Nature, 183, 1801(1959)
(b) G. Herzberg, Can. J. Phys., 39, 1511(1961)
(c) G. Herzberg, Proc. Roy. Soc. (London), A262, 291(1961)
16. H. M. Frey, J. Am. Chem. Soc., 82, 5947(1960)
17. J. W. Simons, B. S. Rabinovitch and D. W. Setser, J. Chem. Phys., 41, 800(1964)
18. D. F. Ring and B. S. Rabinovitch, J. Am. Chem. Soc., 88, 4285(1966)
19. (a) K. R. Kopecky, G. S. Hammond and P. A. Leermakers, ibid., 84, 1015(1962)

19. (b) K. R. Kopecky, G. S. Hammond and P. A. Leermakers, ibid., 83, 2397(1961)
20. W. von E. Doering and H. Prinzback, Tetrahedron, 6, 24(1959)
21. F. J. Duncan and R. J. Cvetanovic, J. Am. Chem. Soc., 84, 3593(1962)
22. (a) R. J. Crawford and A. Mishra, ibid., 88, 3962(1966)
(b) L. Ali, M.Sc. Thesis, Univ. of Alta., 1967.
(c) G. Erickson, M.Sc. Thesis, Univ. of Alta., 1966.
(d) A. Mishra, Ph.D Thesis, Univ. of Alta., 1965.
23. K. L. Rinehart, Jr., and T. V. VanAuken, J. Am. Chem. Soc., 82, 5251(1960)
24. T. V. VanAuken and K. L. Rinehart, Jr., ibid., 84, 3136(1962)
25. (a) D. E. McGreer, R. S. McDaniel and M. G. Vinje, Can. J. Chem., 43, 1389(1965)
(b) D. E. McGreer, N. Chiu, M. G. Vinje and K. C. Wong, ibid., 43, 1407(1965)
(c) D. E. McGreer, N. Chiu and M. G. Vinje, ibid., 43, 1398(1965)
26. P. Kozak, Ph.D. Thesis, Univ. of Alta. 1964.
27. (a) J. A. Bell, Prog. in Phys. Org. Chem., Vol. 2, 1(1964)
(b) J. A. Bell, J. Am. Chem. Soc., 87, 4966(1965)
28. R. J. Cvetanovic, H. E. Avery and R. S. Irwin, J. Chem. Phys., 46, 1993(1967)
29. B. C. Roquitte, J. Phys. Chem., 70, 1334(1966)
30. F. E. Blacet and A. Miller, J. Am. Chem. Soc., 79, 4327(1957)
31. (a) R. Srinivasan, Adv. in Photochem., Vol. 1, 83(1963)
(b) R. Srinivasan, J. Am. Chem. Soc., 81, 5541(1959)
32. R. F. Klemm, D. N. Morrison, P. Gilderson and A. T. Blades, Can. J. Chem., 43, 1934(1965)
33. R. Hoffmann, Private Communication.

- 34. H. E. Simmons, Private Communication.
- 35. W. R. Roth and M. Martin, Ann., 702, 1(1967)
- 36. A. E. Messner, D. M. Rosie and P. A. Argabright, Anal. Chem., 31, 230(1959)
- 37. W. A. Dietz, J. Gas Chrom., 5, 68(1967)
- 38. G. E. Coates and L. E. Sutton, J. Chem. Soc., 1187(1948)
- 39. N.B. Slater, Unimolecular Reaction Rate Theory, Cornell Univ. Press, Ithaca, 1959

PART II

THE ATTEMPTED SYNTHESIS AND TAUTOMERIZATION RATE
OF 3,4,5,6-TETRAHYDOPYRIDAZINE

CHAPTER I

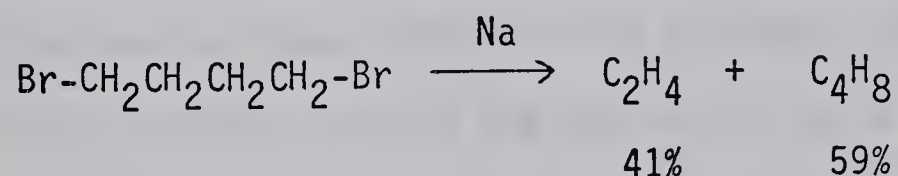
INTRODUCTION

The Tetramethylene Diradical

There is just as much controversy concerning the tetramethylene diradical as there is concerning the trimethylene diradical, however, not as much work has been done in the field of the former, mainly because there is no reaction analogous to methylene addition to olefins for producing a 'hot' cyclobutane or 'hot' diradical.

In 1935, Saltmarsh and Norrish¹ photolyzed cyclopentanone and proposed an intermediate tetramethylene diradical. However, they did not detect any cyclobutane in the products, but this may have been due to inadequate product analysis.

Bawn and Milsted², in 1939, treated 1,4-dibromobutane with sodium vapor and found the following:



They proposed that the reaction proceeded through a tetramethylene diradical which could either cleave to give ethylene or rearrange to give butenes. No cyclobutane was observed in this case but, again, this may have been due to inadequate analysis procedure.

The thermolysis of cyclobutane has been studied fairly extensively.

It has been found that the reaction is homogeneous and first order³, with no induction period and no radical chain process involved. Pritchard et al.⁴ have suggested that the most plausible mechanism for cyclobutane thermolysis is that shown in Scheme I,

SCHEME I

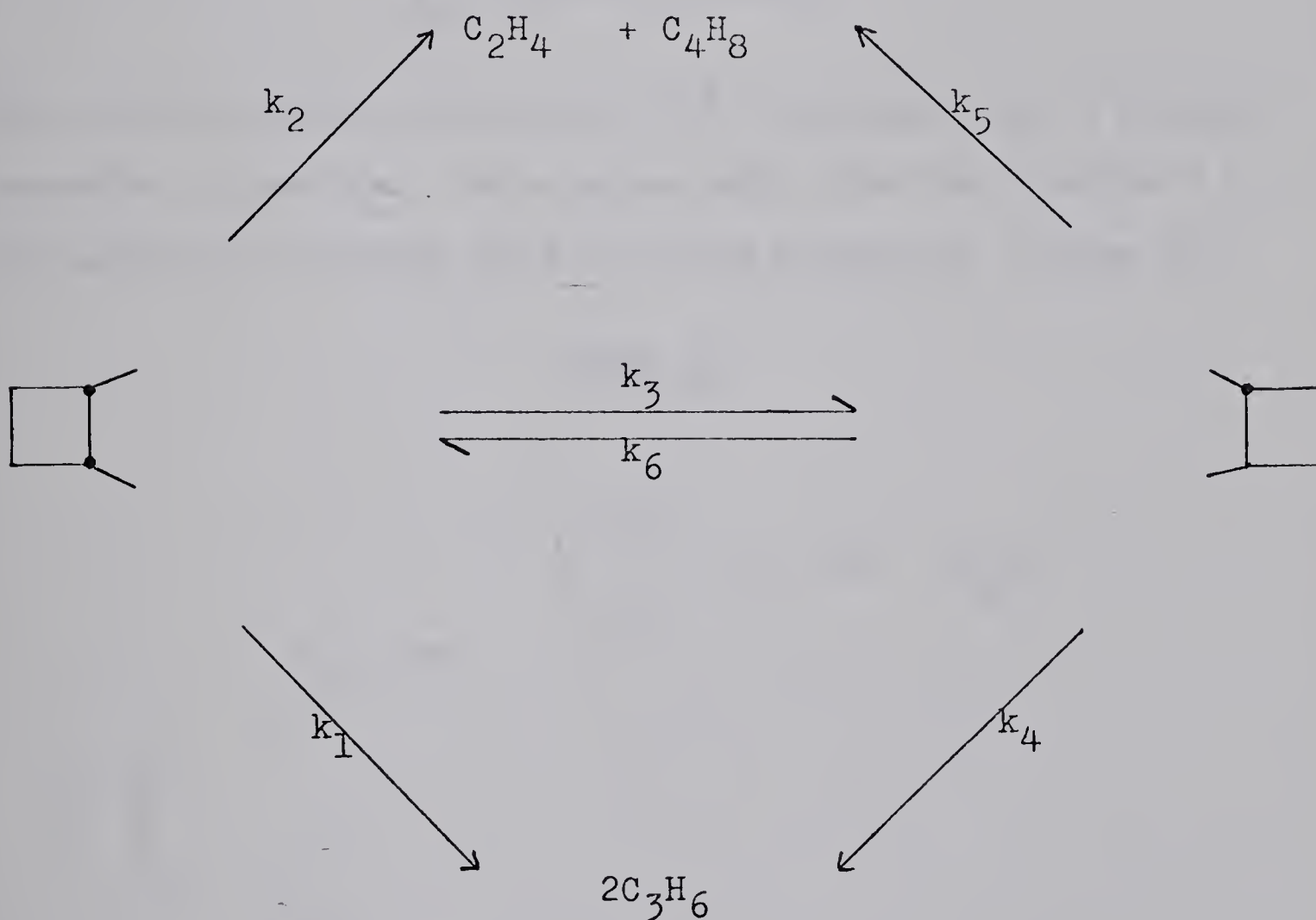


The authors point out that the reaction, like cyclopropane thermolysis, fits Slater theory when H-H distance or C-H distance is taken for the critical reaction coordinate. Kern and Walters⁵ have shown that the reaction is not inhibited by NO, propylene or toluene, and that there are no side reactions taking place. This has been used to rule out the possible intermediacy of a diradical but, Frey⁶ has noted that if the diradical has a very short lifetime similar to that proposed for the trimethylene diradical, no inhibition is expected. A mixture of cyclobutane and cyclobutane-d₈ has been thermolyzed and no cross products were observed. This rules out the possibility of 'free' radicals, but not the possibility of a diradical.

Srinivasan and Kellner⁸ have thermolyzed 1,1,2,2-tetradeuterio-cyclobutane and found ethylene, 1,1-dideuterioethylene and tetradeuterio-ethylene, in a ratio of 1.03:2.02:1.00 respectively. This shows that ethylene produced from the pairing of diagonally opposite methylene groups is a very minor product, if present at all. It does not tell anything about whether the reaction proceeds through a diradical.

In 1961, Gerberich and Walters⁹ reported the thermolysis of cis- and trans-1,2-dimethylcyclobutane. The products found were, cis- and trans-2-butene and propylene. The following reaction scheme was suggested:

SCHEME II



It was found that the decomposition reactions were considerably faster than cis-trans isomerization, in contrast to the thermolysis^{10,11} of 1,2-dimethylcyclopropane. It was also found that,

$$k_1 = 10^{15.48} e^{-60400/RT}$$

$$k_2 = 10^{15.57} e^{-63,000/RT}$$

$$k_3 = 10^{14.81} e^{-60,100/RT}$$

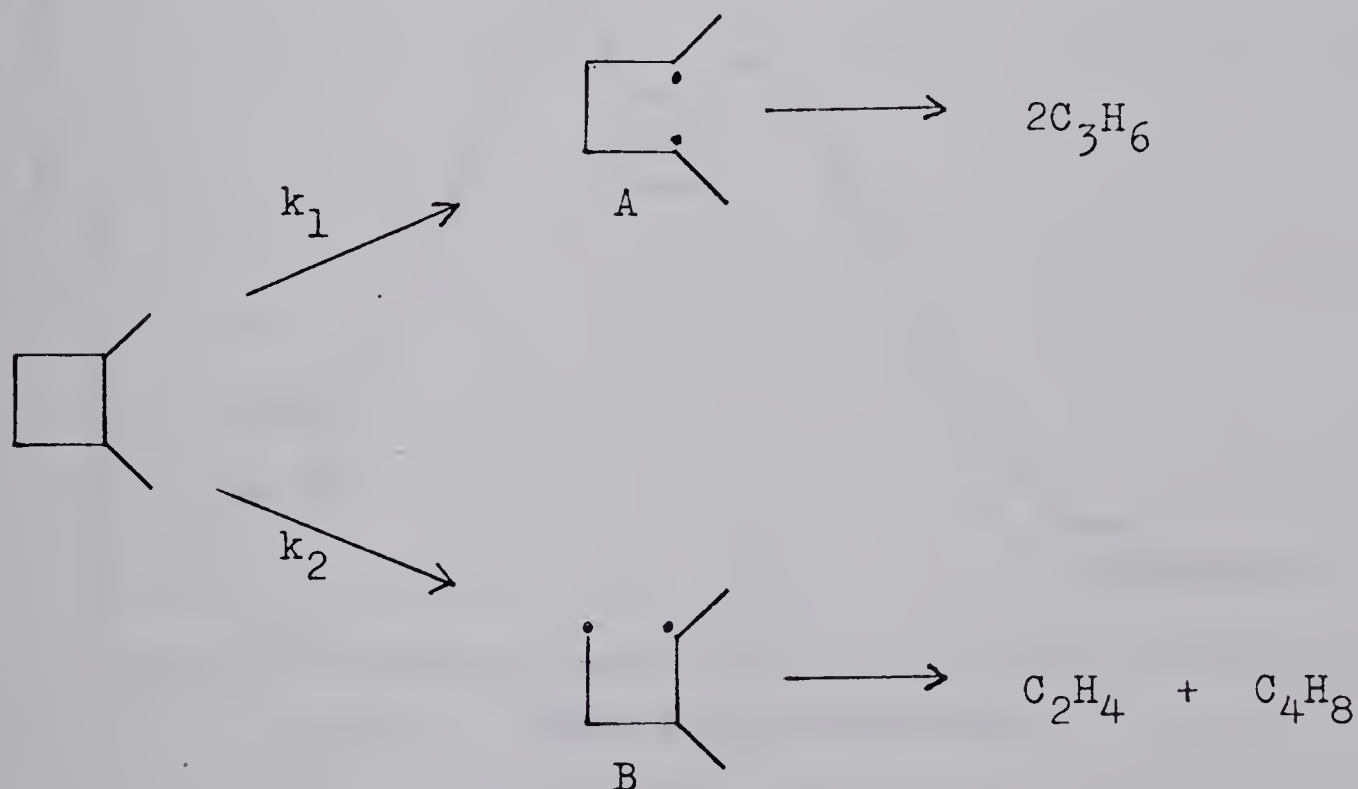
$$k_4 = 10^{15.45} e^{-61,600/RT}$$

$$k_5 = 10^{15.46} e^{-63,400/RT}$$

$$k_6 = 10^{14.57} e^{-61,300/RT}$$

The results have been discussed by Frey⁶, who suggests that a diradical mechanism is plausible. The propylene could arise from diradical A and the butenes plus ethylene could arise from diradical B, (Scheme III).

SCHEME III



Frey argues that the difference in activation energy for k_1 and k_2 should reflect the difference in stability between a primary radical and a secondary one and suggests that the values of 2.6 kcal/mole (cis) and 1.8 kcal/mole (trans) are quite reasonable. Frey also states that if a diradical is involved, the energy profile for the reaction must be as shown in Figure 1, to explain decomposition being faster than cis-trans isomerization.

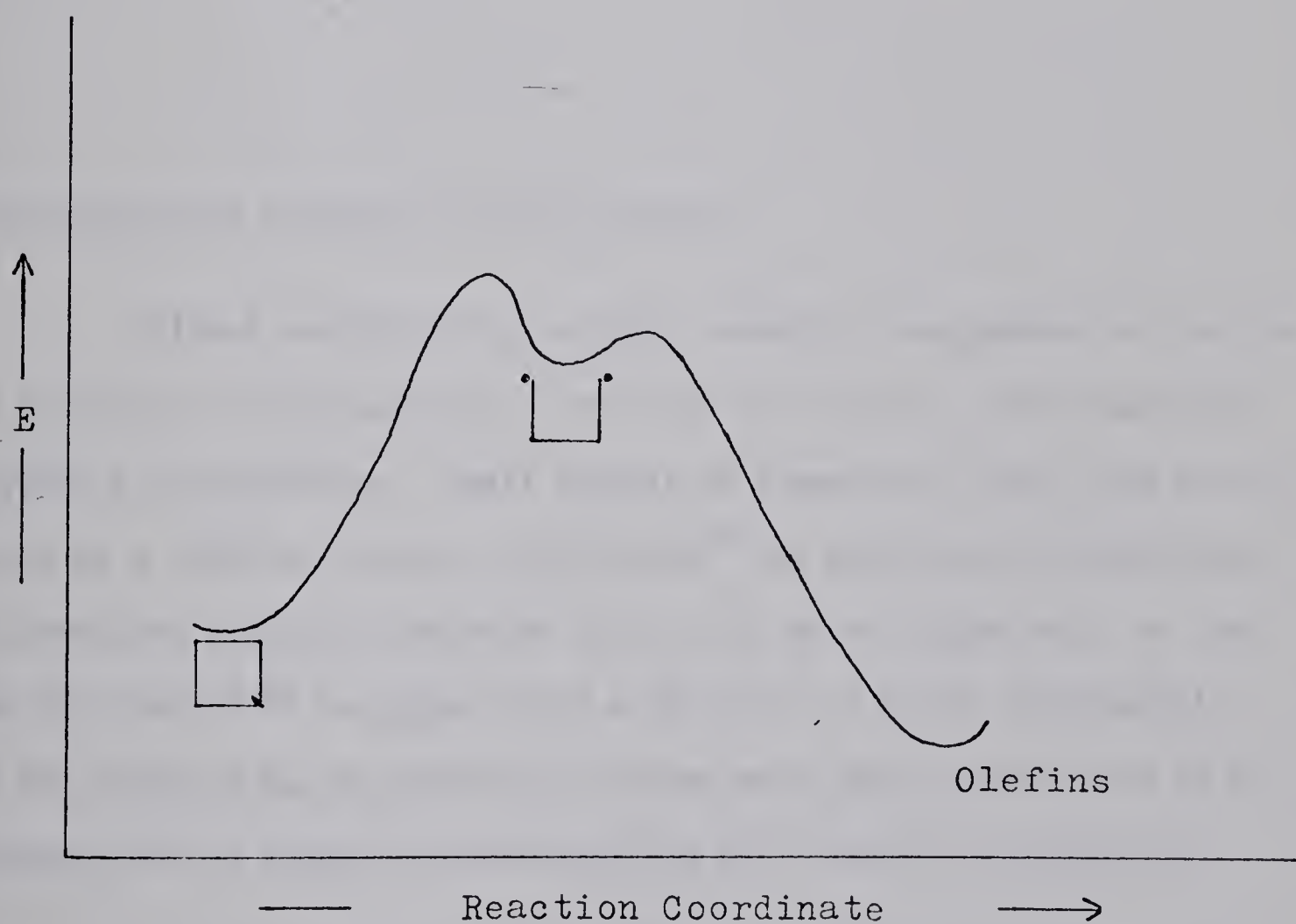
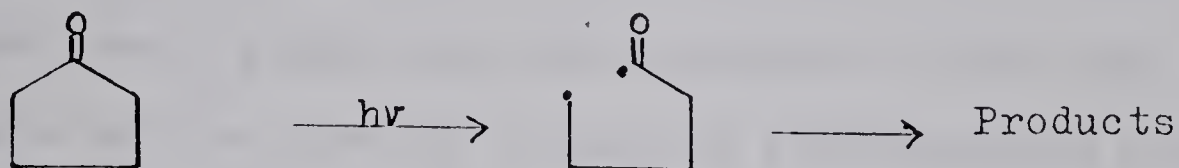


FIGURE 1

A definite conclusion on the mechanism of thermolysis of cyclobutanes is impossible since either a mechanism of the type shown in Scheme I

or one shown in Scheme III may equally well account for the results.

In 1942, Benson and Kistiakowsky¹² reported the photolysis of cyclopentanone and proposed a diradical of the type,

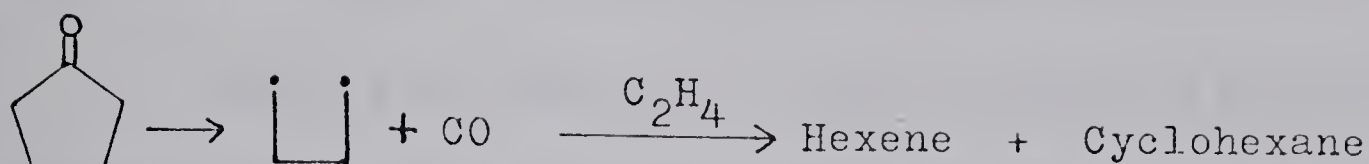


A tetramethylene diradical was not proposed.

Blacet and Miller¹³, in 1957, reported a comprehensive study on the photolysis of cyclopentanone and found as products, carbon monoxide, ethylene and cyclobutane. Small amounts of 4-pentenal¹⁴ have also been reported as a reaction product. Srinivasan¹⁶ has photolyzed cyclopentanone and found the products unaffected by up to 35 mm of oxygen gas. He then used this data^{15,16} to suggest that a diradical is not an intermediate. All the products may be explained in other ways, and the inertness of the intermediates to oxygen is not compatible with radical intermediates.

In 1959, Flowers and Frey¹⁷ found hexene and cyclohexane as products when cyclopentanone was photolyzed in the presence of ethylene. To explain this they proposed,

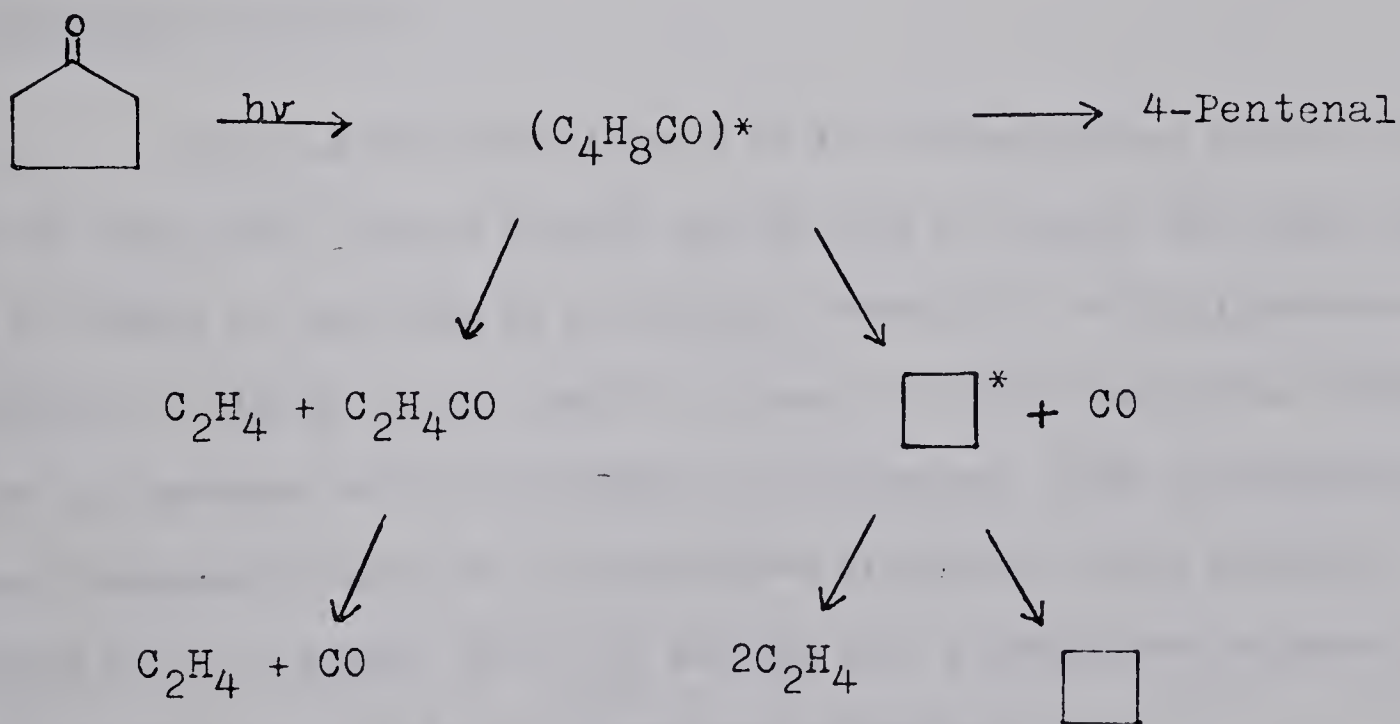
SCHEME IV



However, the C_6 products may also be explained in other ways, and their presence does not prove the existence of a tetramethylene diradical.

Klemm et al.^{18a} could not repeat the foregoing result of Flowers and Frey, so the issue of whether cyclopentanone photolysis produces the tetramethylene diradical remains very much in doubt. Most authors do not favor the tetramethylene diradical but, instead, favor a mechanism similar to that put forward by Klemm and co-workers, (Scheme V).

SCHEME V



The authors do not conclude anything about the nature of the (C_4H_8CO), but suggest that a diradical type species is consistent with the products.

Woodward and Hoffmann^{18b}, in their treatment of electrocyclic reactions, concluded that a one-step process for the formation of cyclobutane from two ethylene molecules was thermally not allowed. By the principle of microscopic reversibility the one-step conversion of cyclobutane to ethylene should also not be allowed thermally. Since the decomposition of cyclobutane to ethylene is a known thermal reaction, then it follows that it should be a multi-step process if Woodward and Hoffmann's computations are correct. The simplest multi-step process for cyclobutane decomposition would be ring opening to give a tetramethylene diradical followed by another carbon-carbon bond cleavage to yield ethylene. So far, there is no experimental evidence for the intermediacy of the tetramethylene diradical in this reaction.

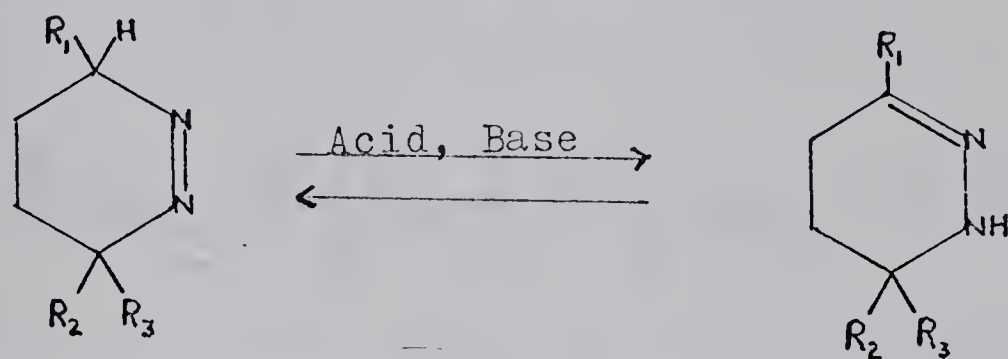
Tetrahydropyridazines

Evidence for the existence of the tetramethylene diradical has so far been sadly lacking (except for the work of Flowers and Frey, which is in doubt) in the cases of cyclobutane thermolysis and cyclopentanone photolysis, similar to the lack of evidence for the trimethylene diradical when cyclopropane and cyclobutanone are decomposed. What is required is some independent source of tetramethylene diradicals, and a suitable system for this appears to be, by analogy with 1-pyrazoline decomposition, the decomposition of 3,4,5,6-tetrahydropyridazines.

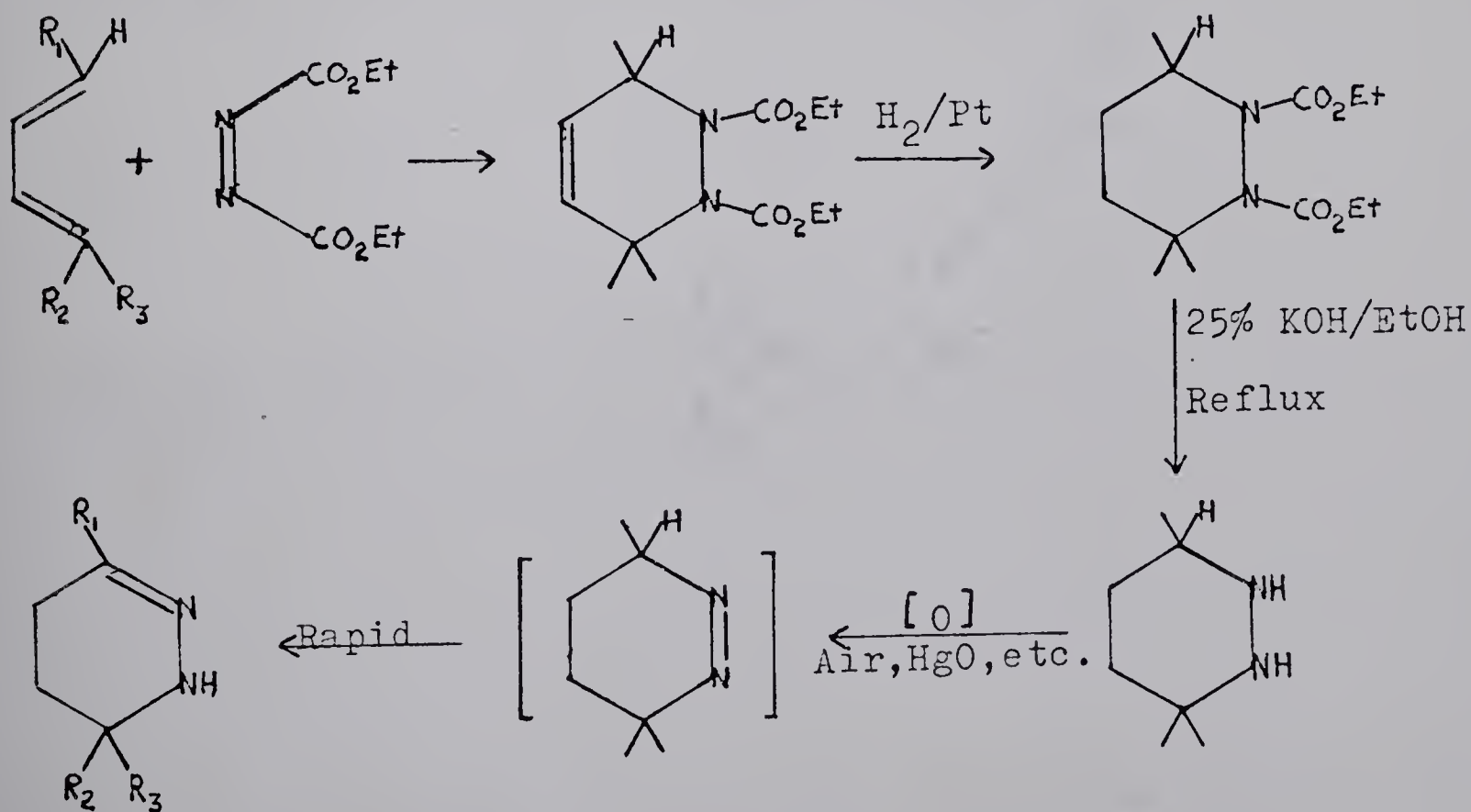
Very few examples of 3,4,5,6-tetrahydropyridazines are reported in the literature¹⁹. Many workers have attempted to prepare them, but

most have only succeeded in isolating the tautomeric hydrazone. The azo compound tautomerizes very rapidly (Scheme VI), and only in certain favorable cases with great experimental care have the azo compounds been isolated.

SCHEME VI

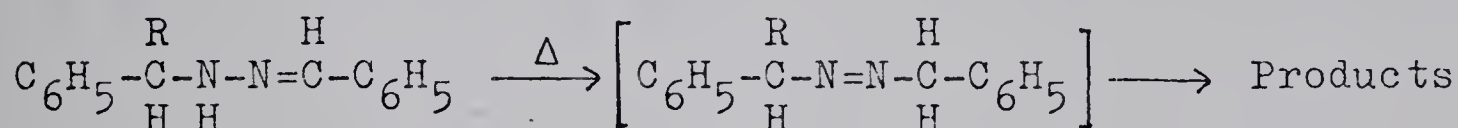


The hydrazones, B, are prepared very simply starting with a Diels-Alder²⁰ reaction as follows^{19,21,25}:

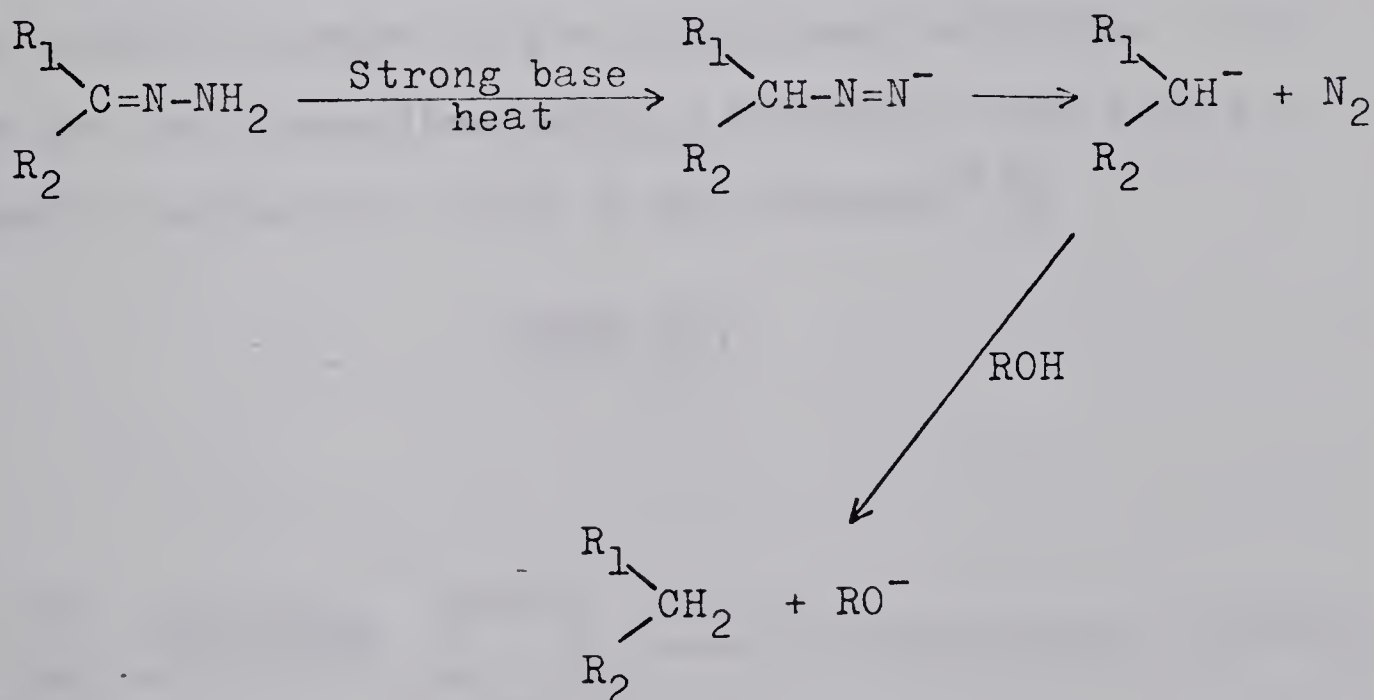


Five membered azo rings are known to be quite stable to hydrazone formation, although they are known to tautomerize under certain conditions²². Likewise, seven membered azo rings, which are fairly easily prepared and handled, also tautomerize slowly²³.

The equilibrium between an azo compound and its tautomer had been proposed as early as 1910²⁴, for the following:

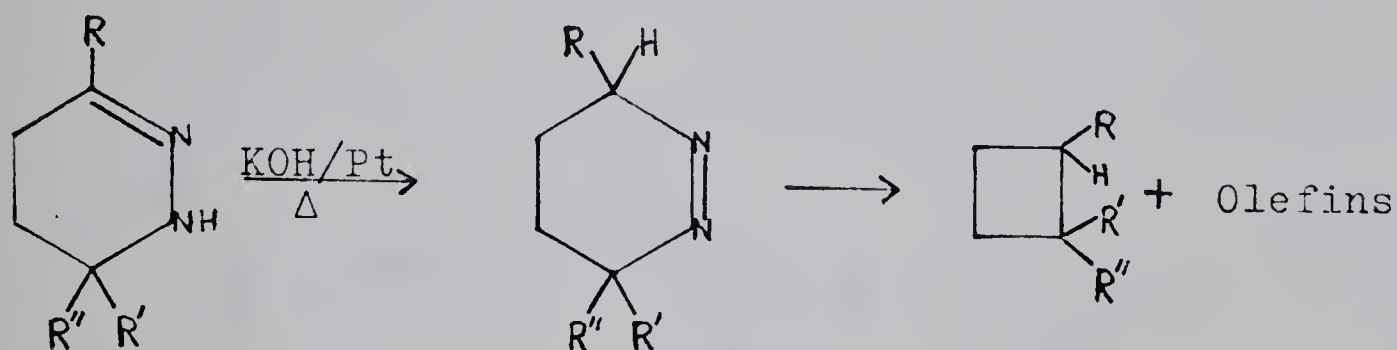


This type equilibrium has been utilized in many instances, the best known of which is probably the Wolff-Kischner reduction.



Levina and co-workers²⁵ have made extensive use of tetrahydro-pyridazine decomposition to prepare cyclobutanes as in the following Scheme:

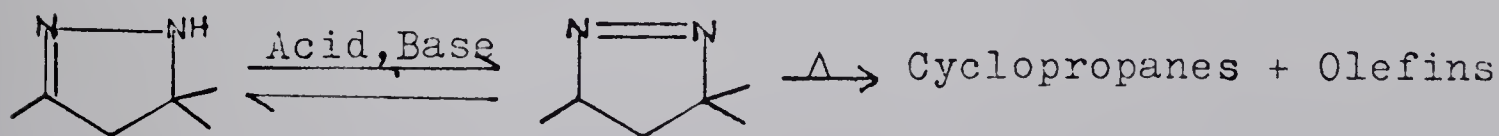
SCHEME VII



Open chain hydrazones and very large azo rings are in equilibrium with the azo compounds, a fact which has been observed^{24,26}.

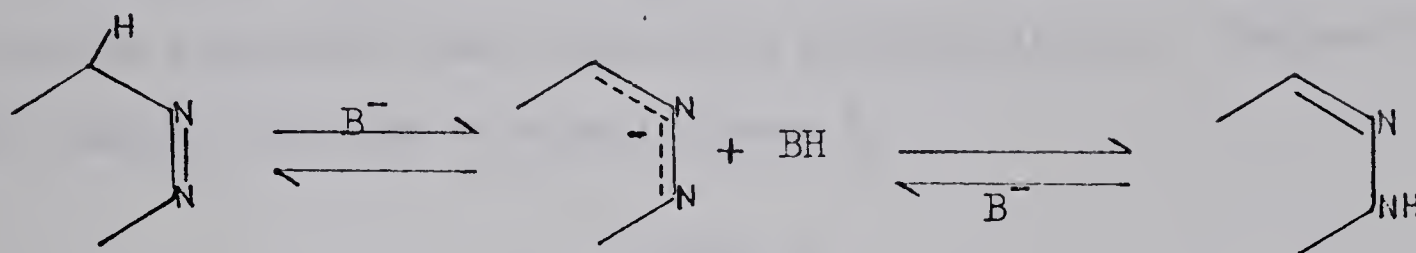
2-Pyrazolines, upon strong heating and/or in the presence of suitable catalysts, decompose to give cyclopropanes and olefins. It is believed that the 2-pyrazolines undergo a prototropic shift to give the corresponding 1-pyrazolines, which in turn decompose^{27,28}.

SCHEME VIII



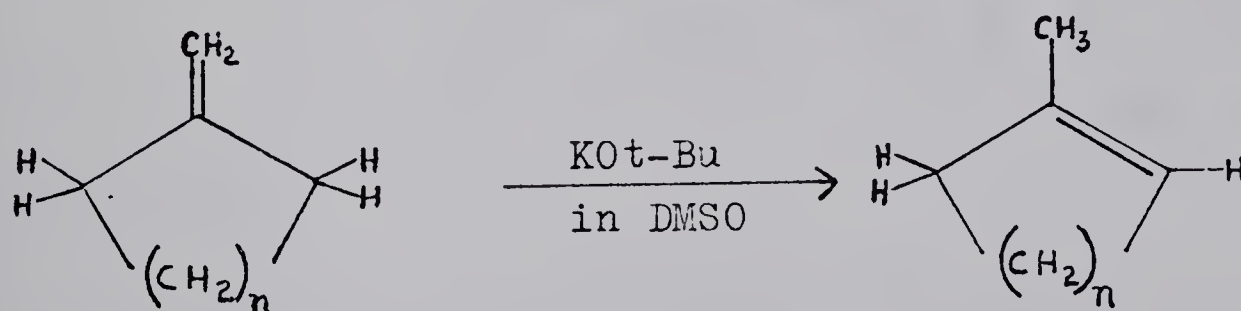
The intermediate for the foregoing tautomerizations is quite probably an ion of the following type:

SCHEME IX



If Scheme IX is correct, then the reaction may be similar to the base catalyzed exo-endo tautomerization of methylenecycloalkanes³⁰ shown in Scheme X.

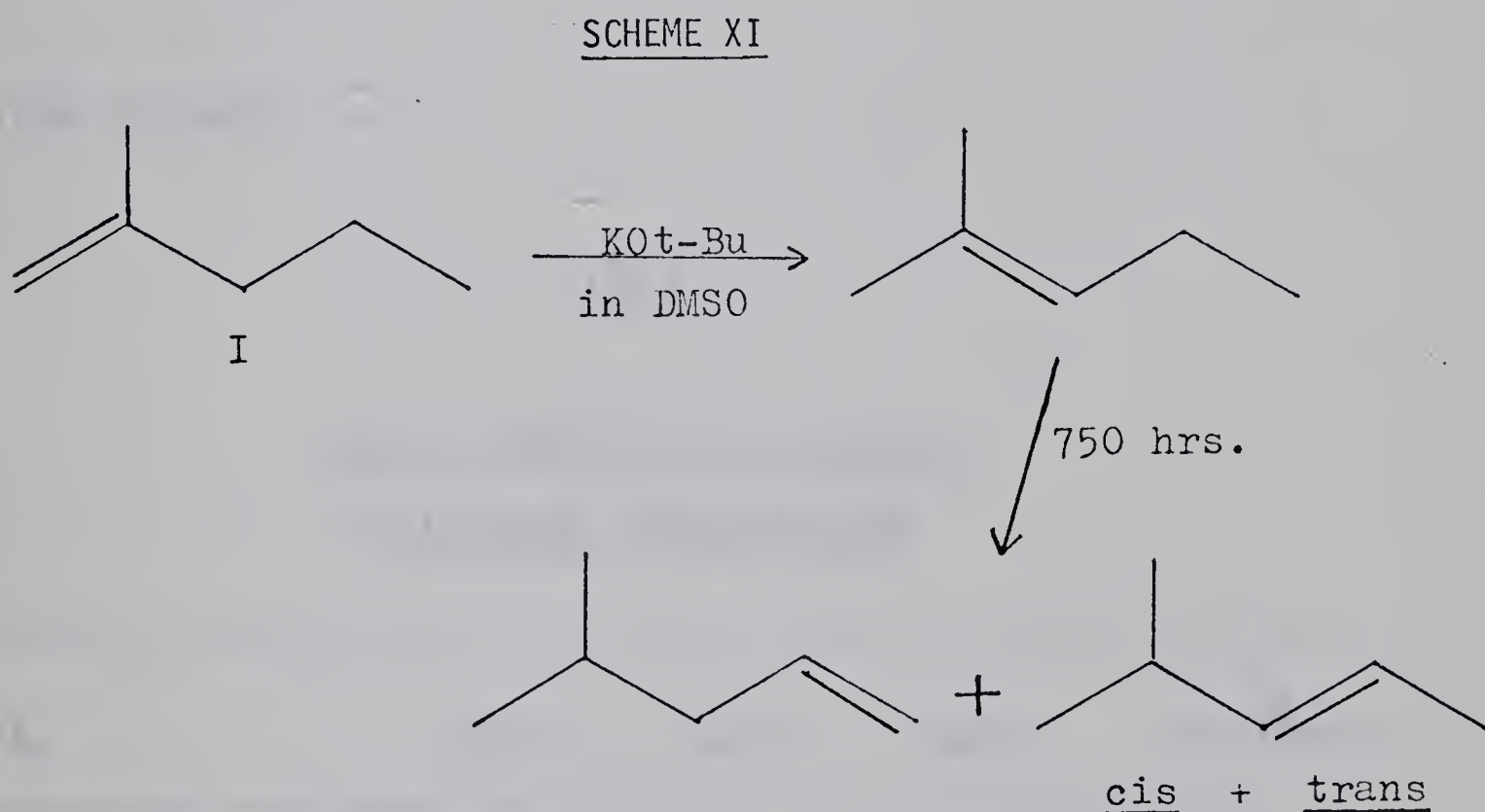
SCHEME X



However, it has been found that for six-membered rings ($n=3$), the rate of tautomerization is slower than either four, five, seven or 8-membered

rings. A similar result is obtained for the bromination of cycloalkanones^{30f}.

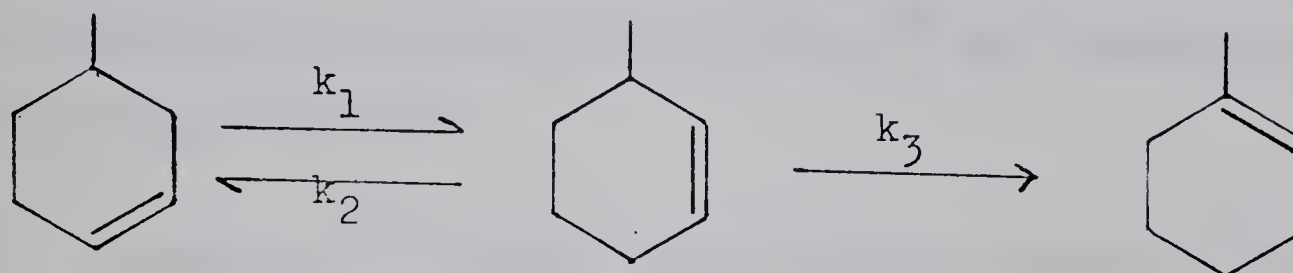
A better model for comparison is probably the base catalyzed tautomerization of olefins. Schriesheim and co-workers³⁰ have studied the kinetics of tautomerization in such olefins as 1-butene and 2-methyl-1-pentene using potassium t-butoxide in dimethylsulfoxide. The reaction for 2-methyl-1-pentene is shown in Scheme XI.



It was found that for the initial disappearance of I, $E_a = 22.0$ kcal/mole and $\Delta S^\ddagger = -16.7$ e.u. It was concluded that the rate determining step is the abstraction of allylic hydrogen by the base and that all systems studied, "point to a preferred conformation consisting of base, solvent

and olefin,"^{30b} for the transition state.

Turksma et al.²⁹ have studied the tautomerization of 4-methylcyclohexene under similar conditions. Their results for,



are given in Table 1.

TABLE 1

KINETIC PARAMETERS FOR 3-METHYL-
CYCLOHEXENE TAUTOMERIZATION

$T^{\circ}\text{K.}$	343.9	352.9	363.0	E_a kcal/mole
$k_1, \text{sec}^{-1} \times 10^6$	3.1	9.3	16.7	18.5
$k_2, \text{sec}^{-1} \times 10^6$	5.3	15.5	29.9	16.9
$k_3, \text{sec}^{-1} \times 10^6$	0.8	2.3	3.5	16.7

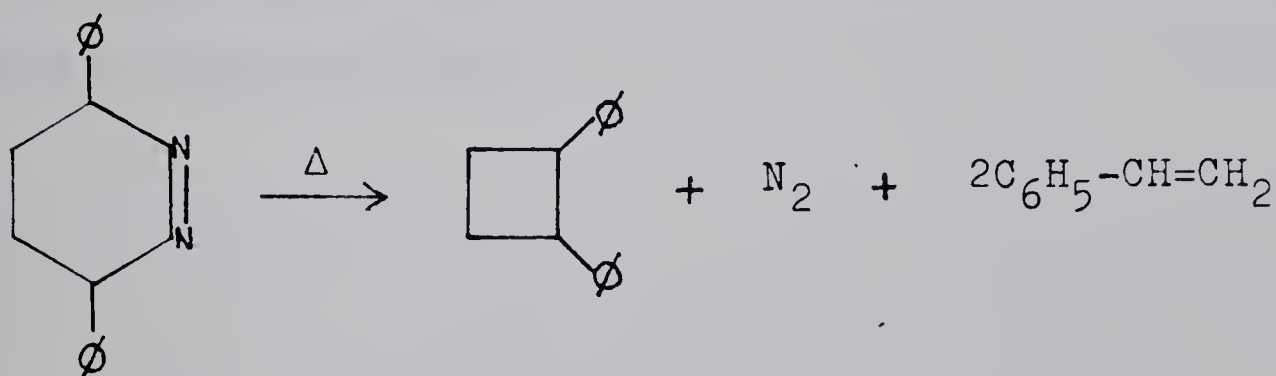
All the foregoing base catalyzed tautomerizations (except methylenecyclohexane) are characterized by high negative entropies of activation which

presumably reflects a highly restricted transition state.

The ease with which the foregoing prototropic rearrangements take place undoubtedly is responsible for the lack of reported 3,4,5,6-tetrahydropyridazines. Only two have been characterized to any extent to date, 3,6-diphenyl-3,4,5,6-tetrahydropyridazine^{19a} and 3,6-dimethyl-3,4,5,6-tetrahydropyridazine^{19c}.

Wang et al.^{19a} prepared the 3,6-diphenyl compound and found λ_{\max} 387m μ , on standing the absorption slowly disappeared to give rise to a new peak, λ_{\max} 292m μ , undoubtedly due to the hydrazone. On thermally decomposing the 3,6-diphenyl-3,4,5,6-tetrahydropyridazine, the products were found to be styrene and 1,2-diphenylcyclobutane, (Scheme XII).

SCHEME XII



The authors proposed an intermediate diradical (Figure 2) for the reaction because it was found that styrene was polymerized if present. The 3,6-dimethyl-3,4,5,6-tetrahydropyridazine could not be worked with to any extent

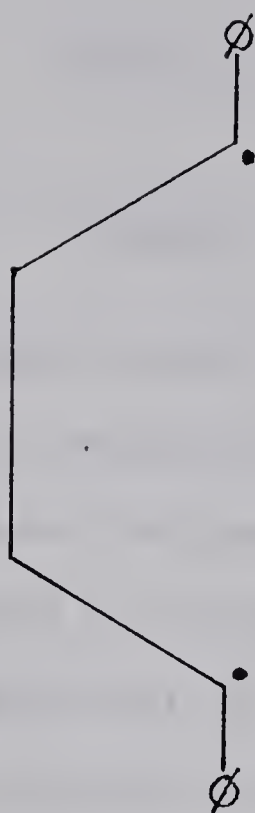


FIGURE 2

and about all that was characterized was its u.v. spectrum - λ_{max} 382 μ m, $E = 112$. After several days this peak disappeared and two new maxima appeared at 318 $m\mu$ and 248 $m\mu$.

CHAPTER II

PROPOSAL

In view of the recent success in the study of trimethylene diradicals³¹ prepared from the decomposition of 1-pyrazolines, it appears worthwhile to attempt to prepare the corresponding six membered analogs (3,4,5,6-tetrahydropyridazines) as a route to tetramethylene diradicals^{19a}. Knowledge of tetramethylene diradicals is in approximately the same state now as was that concerning trimethylene diradicals before studies on methylene addition to olefins and pyrazoline decompositions.

An independent source of tetramethylene diradicals is desirable in order to compare properties observed in cyclobutane thermolysis and cyclopentanone photolysis.

Difficulty preparing 3,4,5,6-tetrahydropyridazine is anticipated because of the previously observed rapid prototropic shift in similar molecules. However, if it can be prepared in sufficient purity, an attempt will be made to perform some experiments on its rate of tautomerization and compare it with the rate of some other azo compounds. It would be interesting to determine why the 1-pyrazolines should be so stable to tautomerization compared to the tetrahydropyridazines.

CHAPTER III

RESULTS AND DISCUSSION

(A) ATTEMPTED SYNTHESIS OF 3,4,5,6-TETRAHYDROPYRIDAZINE.

Many attempts were made to find a suitable method for the oxidation of hexahydropyridazine(1) prepared according to the method of Baranger et al.^{21a}, from ethyl azodicarboxylate and butadiene, etc., to 3,4,5,6-tetrahydropyridazine(2). The first attempt employed silver oxide in methanol. but the product after distillation showed little azo absorption (300-400m μ) in the u.v. A second attempt by bubbling oxygen through a n-hexane solution of 1 produced absorption bonds at 375m μ , 235m μ and 270m μ in the u.v. A third attempt using the procedure of Cohen and Zand^{19c} involving mercuric oxide proved to be the most successful. A mixture of 1 with n-pentane was slowly added to a stirred mixture of mercuric oxide and anhydrous sodium sulfate in pentane at -5°C over a period of about one hour. The pentane was flashed off under reduced pressure and the residue distilled. The ultraviolet spectrum of the distillate (62-65°/23 mm) showed approximately 85% of 2 and 15% of 1,4,5,6-tetrahydropyridazine(3).

To obtain the above percentages, the extinction coefficients of 2 and 3 had to be determined and this was done as follows. A weighed amount of the product was dissolved in a measured volume of n-hexane, and a few drops of glacial acetic acid added. The absorption bond at 375m μ disappeared after several hours while the bond at 235m μ grew larger. By

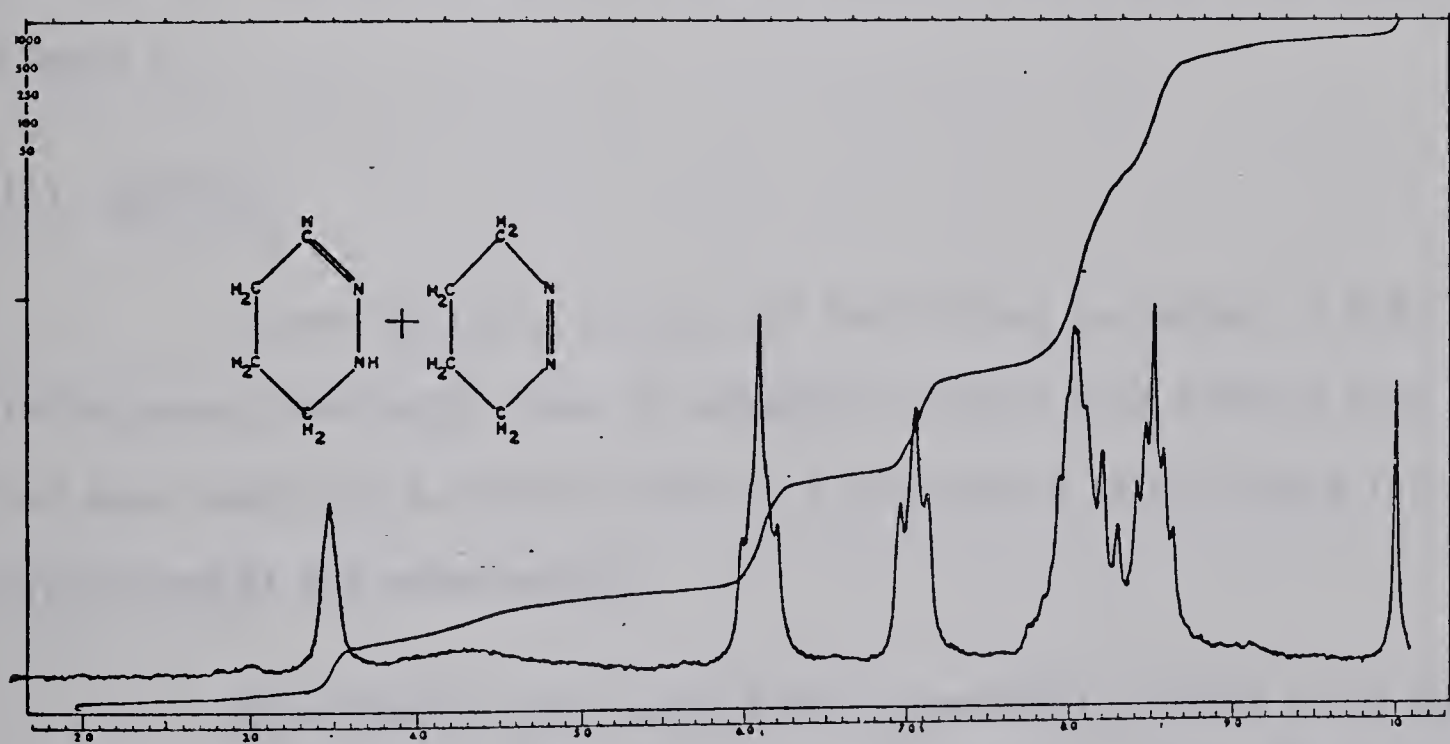
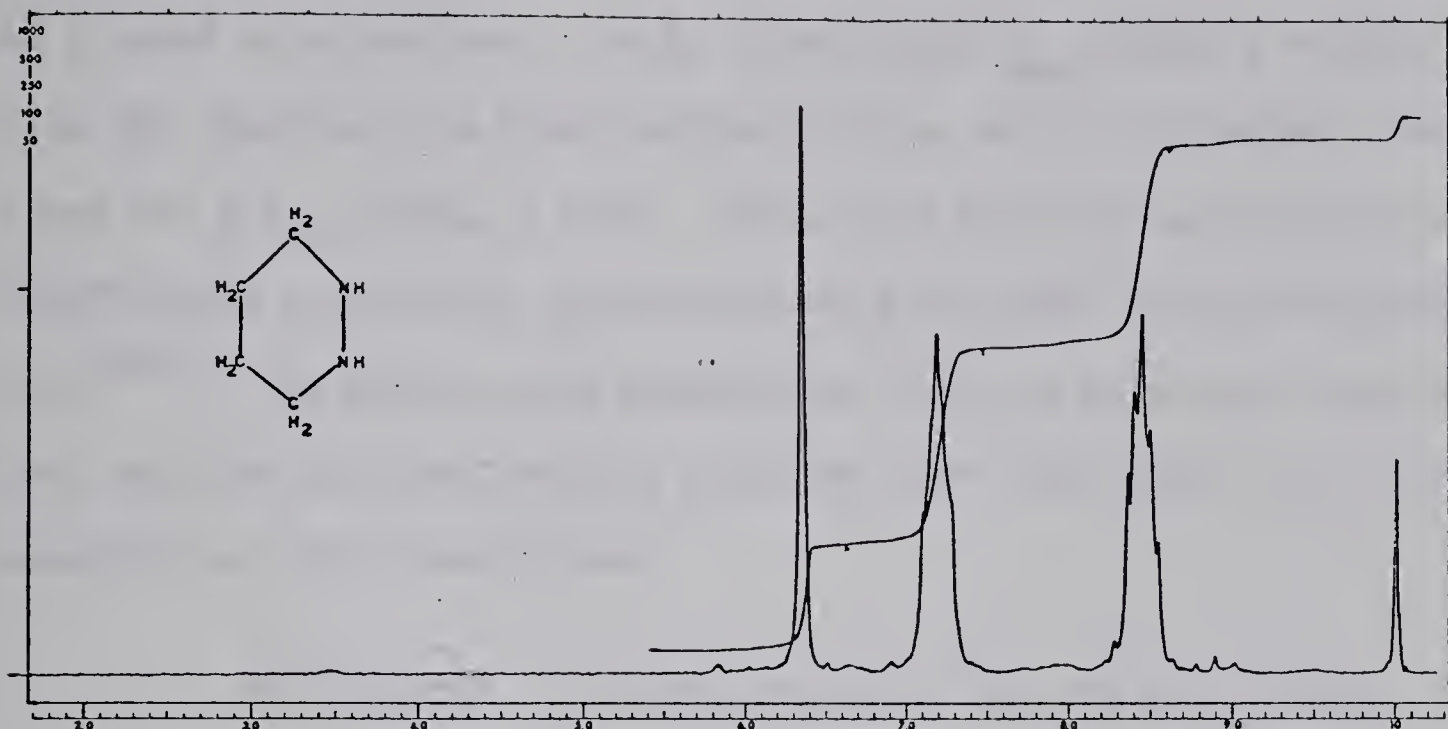


FIGURE 3

assuming that the distillate originally contained only 2 and 3, and that the acetic acid converted all the 2 into 3, the extinction coefficient of 3 could be determined. For 3, it was found λ_{max} 235m μ , ϵ = 3290. From the spectrum of a fresh solution with no acetic acid added it was found for 2, λ_{max} 375m μ , ϵ = 219. These band positions and extinction coefficients are similar to those reported for other tetrahydropyridazines^{19a,c}. The position and magnitude of the long wavelength band is that expected for azo linkages, while the short wavelength band is that expected for -C=N- absorptions.

All attempts to rid the product of the 15% of 3 failed. The azo compound, 2, would tautomerize too quickly under all purification conditions. The nmr spectra of 1 and a mixture of 2 and 3 are shown in Figure 3.

(B) KINETICS

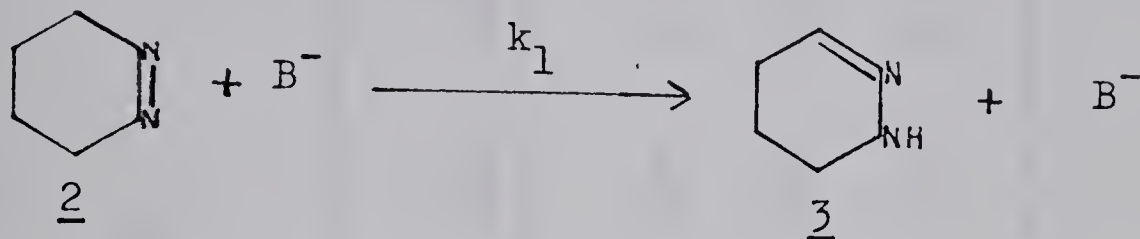
It was decided, in spite of the failure to prepare 3,4,5,6-tetrahydropyridazine(2) pure, to attempt to obtain some kinetic data on the base catalyzed tautomerization of 2 and compare it with data for 1-pyrazoline(4) and azoethane(5).

Rate studies were carried out in methanol solvent using sodium methoxide as the base. Three temperatures were used (20°, 30° and 40°C), with varying base concentrations for each compound. The data were obtained by following the disappearance of the azo band of each compound spectrophotometrically in an ultraviolet spectrophotometer (Carey, 14M) with a cell compartment thermostatted with water from a Colara constant temperature bath. The reaction was shown to be first order in azo compound and first

order in base. The base concentration remained constant throughout the course of the reaction.

The data were treated as follows:

For



$$\begin{aligned}
 \frac{-d[\underline{2}]}{dt} &= k_1 [\underline{2}] [\text{B}^-] \\
 &= k' [\underline{2}] \quad \text{where } k' = k_1 [\text{B}^-]
 \end{aligned}$$

Integration gives,

$$\ln[\underline{2}] = -k't + C$$

$$\text{Since } [\underline{2}] = a_2 \times \text{constant}$$

where a_2 = absorbance of $\underline{2}$

Therefore

$$2.303 \log(a_2) = -k't + C'$$

A plot of $2.303 \log (\text{absorbance})$ vs. time yields k' . On dividing k' by the base concentration we obtain k_1 . The results for the three compounds studied are given in Table 2.

TABLE 2

KINETIC PARAMETERS FOR TAUTOMERIZATION

OF AZO COMPOUNDS

Compound	$k_1^a \times 10^3, \text{ sec.}^{-1}$		LogA	$E_a,$ kcal/mole	$\Delta S_a, \text{ e.u.}$
	20°	30°	40°		
3,4,5,6-Tetrahydro- pyridazine(2)	88.2±2.3	162±2	280±6	10.7±0.3	-26.6±2.1
1-Pyrazoline(4)	0.522±0.012	1.27±0.04	2.97±0.10	15.9±0.6	-19.0±2.0
Azoethane(5)	0.0413±0.0007	0.0968±0.0009	0.227±0.007	15.7±0.2	-24.8±2.1

^aAverage of at least 3 runs at each temperature.

The plots of $\log (a)$ vs. time for 2 and 5 were good straight lines, with a slight trace of curvature after about 75% reaction. The plots for 4 began to curve fairly badly after about 50% reaction. Typical plots for each compound are shown in Figures 4, 5 and 6. The most probable reason for this curvature is that the absorption band for the hydrazone is quite strong, and as the reaction proceeds it may overlap slightly with azo band. This would be manifested to a greater extent in 4 because its azo absorption (λ_{\max} 315m μ) is closer to the -C=N- absorption.

With respect to the above, all rate constants were measured from the data obtained early in the reactions so as to give values as close to the zero time rate constants as possible. Since 2 was only eighty-five percent pure at the start (when solution made up), zero time shown in Figure 3 really represents the point at which about 15 - 25% of the reaction is completed.

The results of Table 2 show that 3,4,5,6-tetrahydropyridazine(3) tautomerizes from 100-170 times faster than 1-pyrazoline(4). This, of course, immediately explains why compounds of this type are difficult to prepare. A reason for the faster rate of 2 could very well be that it has one of its C-H bonds in the 3-positions, almost exactly parallel to the p-orbital of the -N=N- group. This would facilitate overlap of the orbital left behind by the departing hydrogen with the p-orbital of the azo group (See Ref. 30f). Compound 4, however, has no C-H bond parallel to the p-orbital of the azo group, so in order for overlap to occur, some bending of the molecule has to take place. Using this argument, however, it is impossible to explain the extremely slow rate for azoethane.

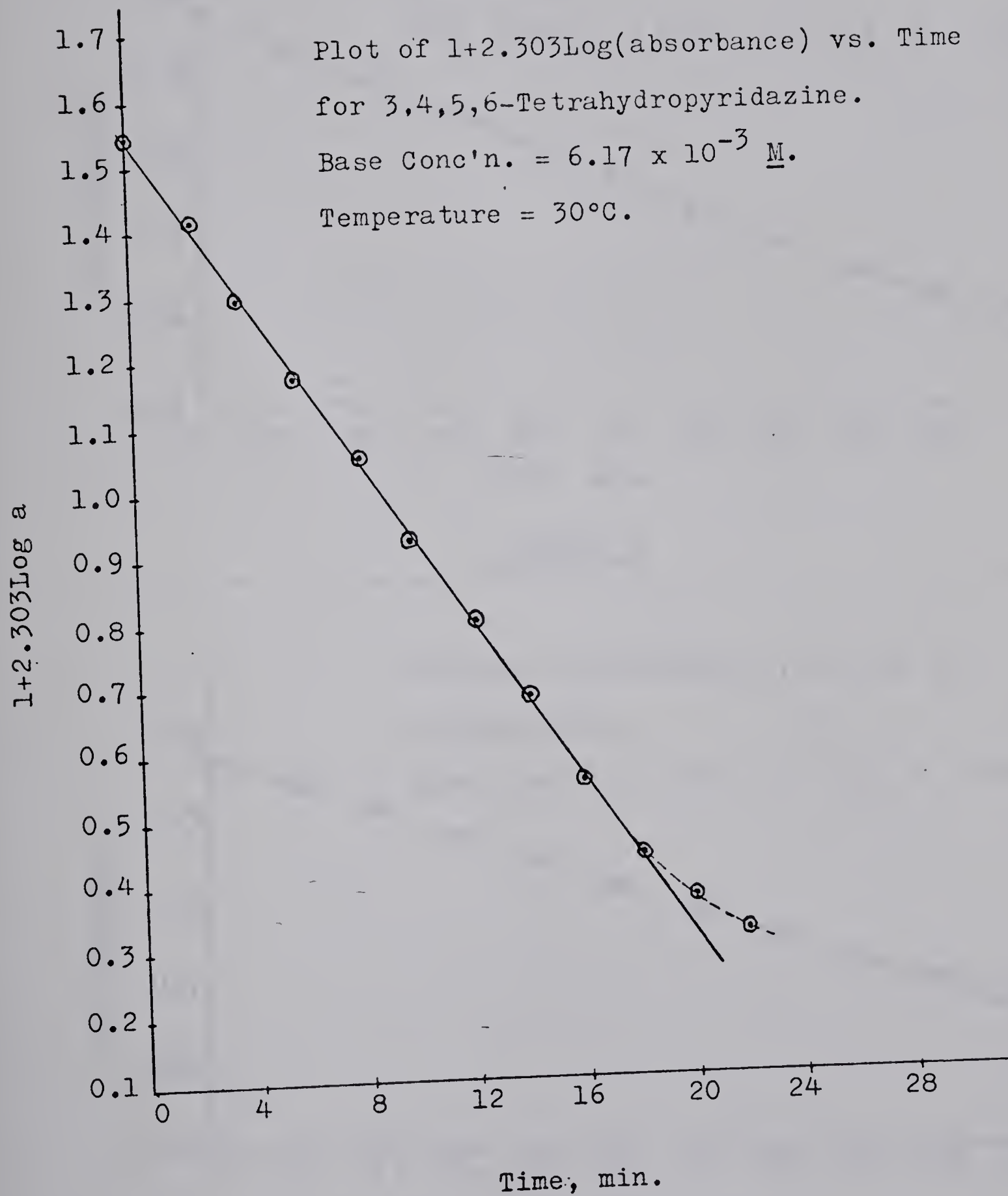


FIGURE 4

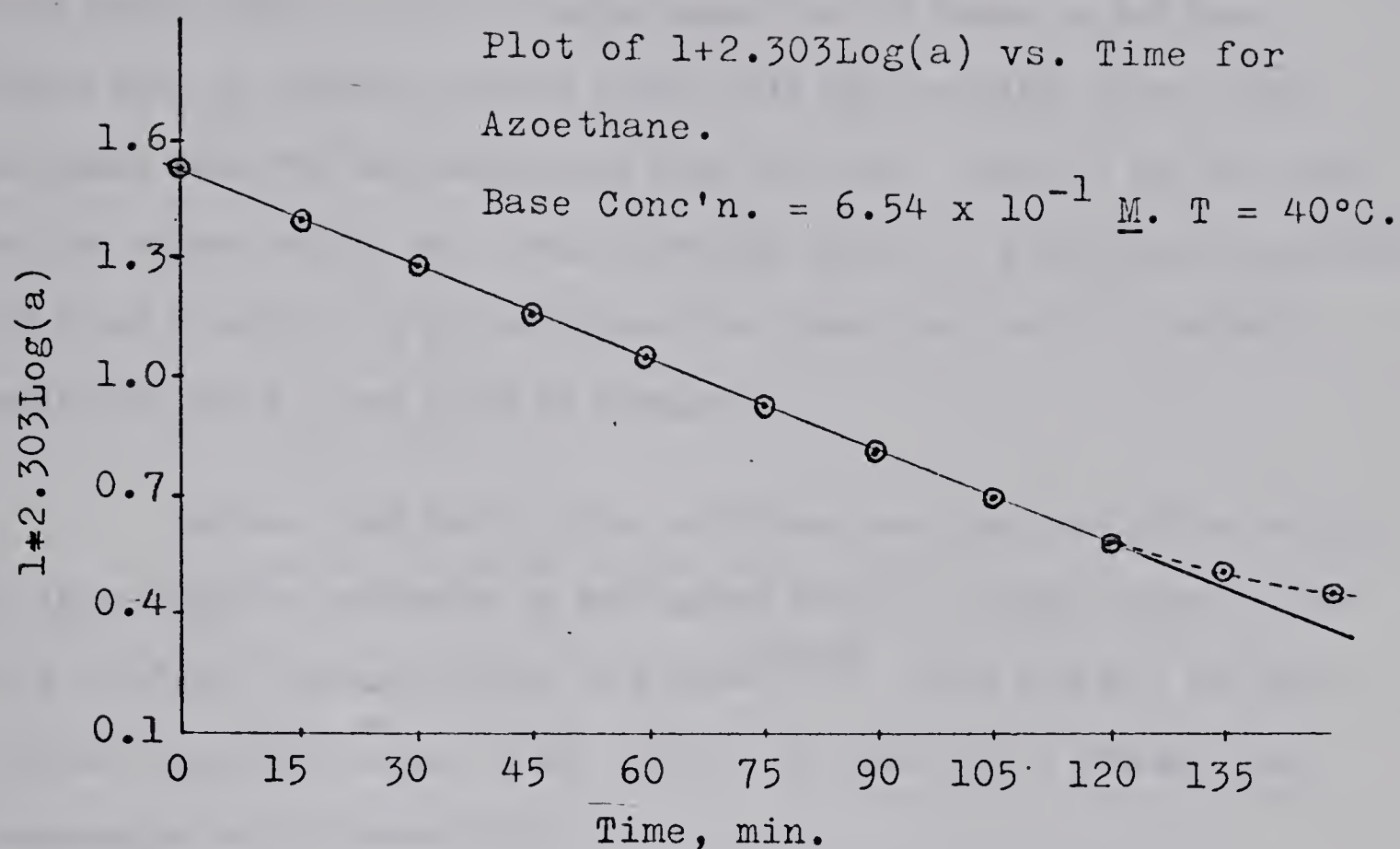


FIGURE 5

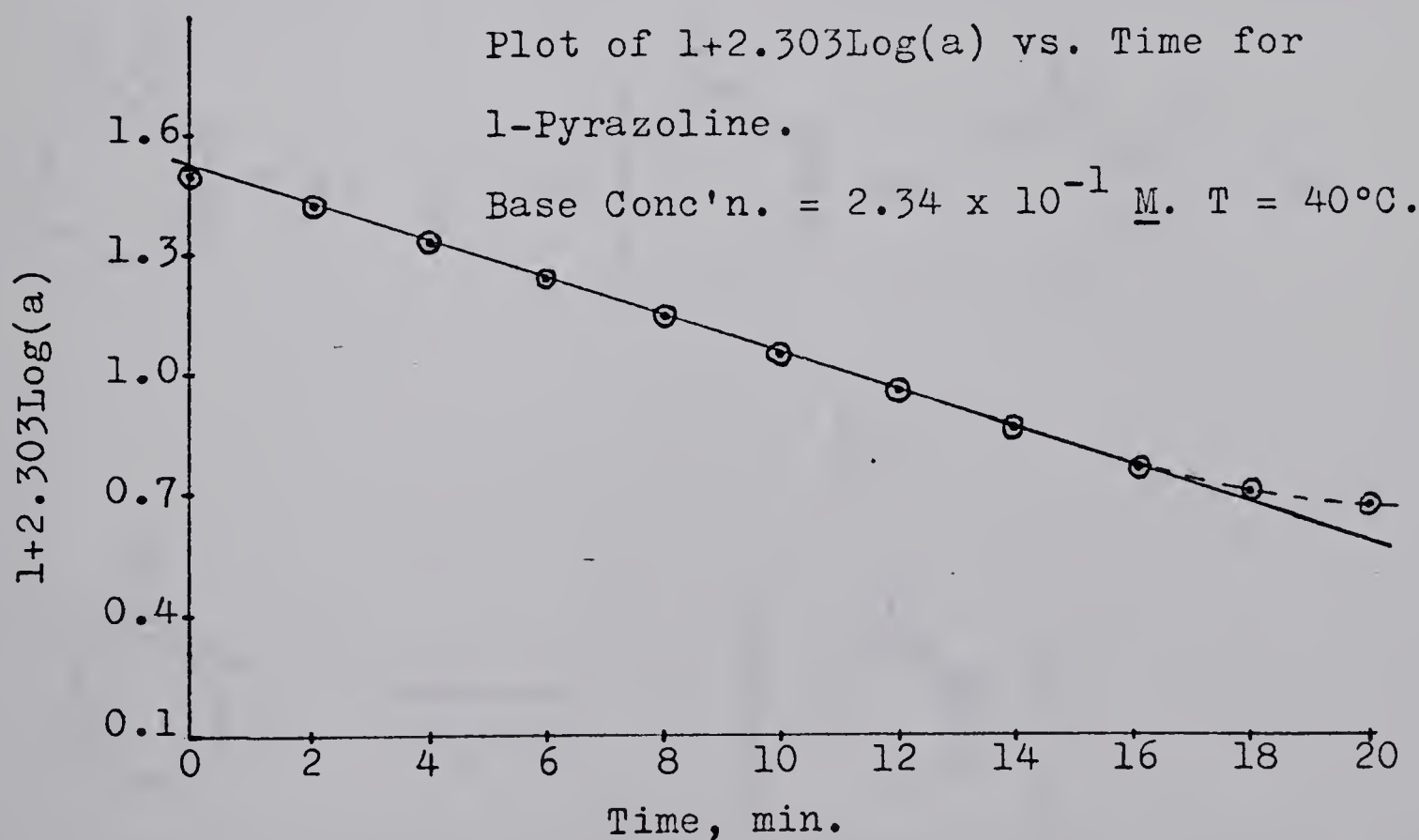
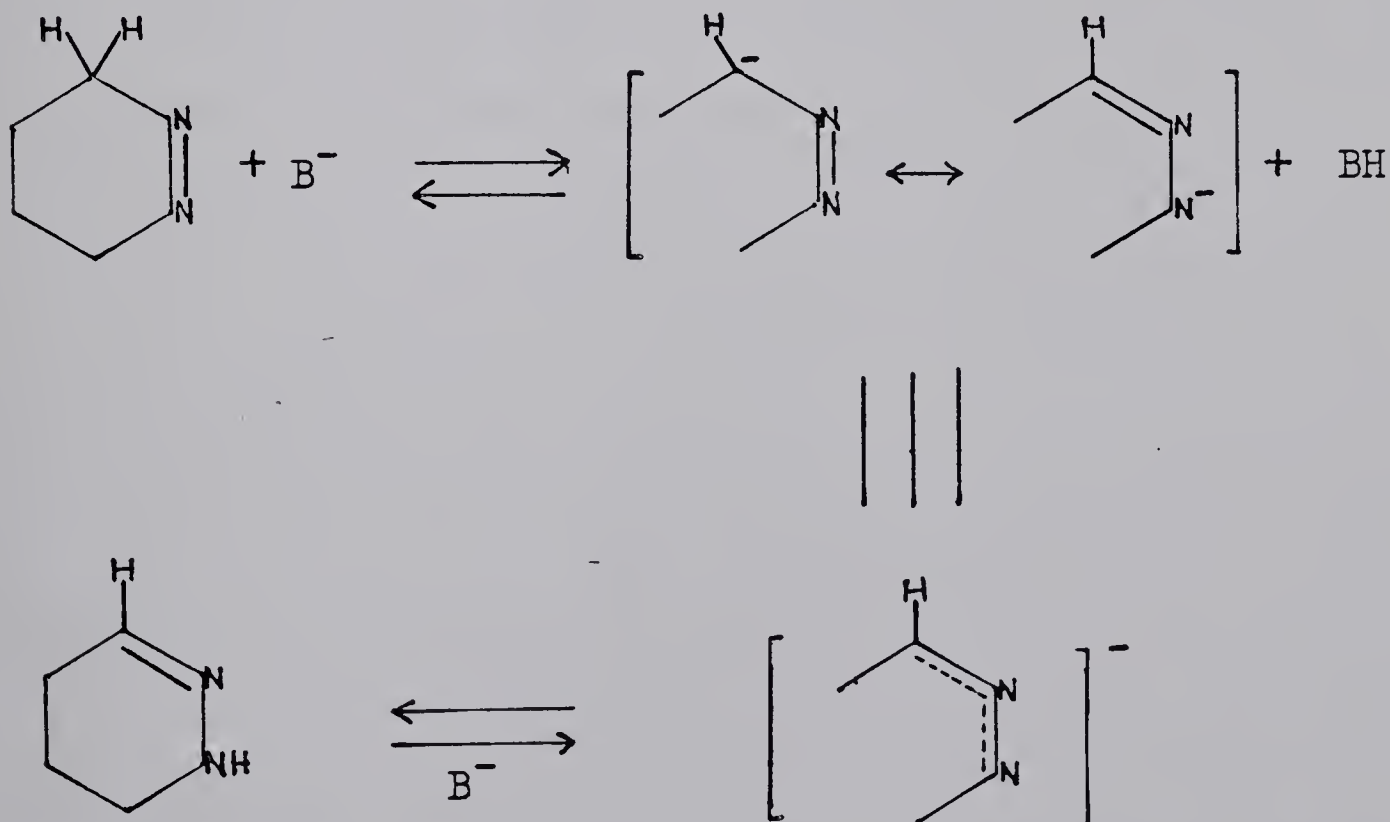


FIGURE 6

Since there should be free rotation about its C-N bonds, a C-H bond should have no trouble aligning itself with the p-orbital of azo group and hence make the tautomerization rate very fast. Such is not the case, and the reason may be that since azoethane exists in a trans-configuration, and 2 and 4 exist in a cis-configuration, then 5 may not be a suitable model with which 2 and 4 can be compared.

We see from Table 2 that all these reactions are characterized by large negative entropies of activation similar to those found for the base catalyzed tautomerization of olefins^{29,30}. This probably reflects similar transition states in all cases. The reaction is probably best represented as in Scheme XIII.

SCHEME XIII



(C) SUMMARY

The tautomerization of azo compounds is probably a similar process to the base catalyzed tautomerization of olefins. Both processes are characterized by large negative entropies of activation probably reflecting similar transition states which are quite restricted compared to the starting compounds.

From kinetic data it is obvious that the preparation of simple 3,4,5,6-tetrahydropyridazines is very difficult due to the very facile prototropic shift which occurs. The secret may lie in getting 2 completely free of any base (either 1 or 3). Since the product of the tautomerization is itself a base, the reaction is expected to be autocatalytic.

CHAPTER IV

EXPERIMENTAL

All infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer, with grating optics. Nuclear magnetic resonance spectra were measured on a Varian Associates A-60 spectrometer using TMS as the internal standard. All ultraviolet spectra were obtained on a Carey Model 14M spectrophotometer. Refractive indices were obtained on a Bausch and Lomb refractometer.

(A) THE ATTEMPTED SYNTHESIS OF 3,4,5,6-TETRAHYDROPYRIDAZINE(2)

(a) Hexahydropyridazine(1), was prepared according to the method of Baranger et al.^{21a}, starting from butadiene and ethyl azodicarboxylate followed by reduction and decarboxylation. A 54% yield of hexahydropyridazine was obtained, based on the starting azodicarboxylate. The Diels-Alder reaction proceeded in over 90% yield followed by reduction in 90% yield. The decarboxylation gave only a 65% yield after final purification. Purification of 1 was effected by distillation through a 5 inch vacuum jacketed column packed with glass helices. B.p. 60-64°/20mm, n_D^{25} 1.4810. Its nmr showed a poorly defined quintet centered at τ 8.45, attributed to the protons in the 4-positions; a poorly defined band centered at τ 7.18, attributed to the protons in the 3-positions; and a sharp singlet at τ 6.34, arising from the protons on the nitrogen atoms. The integrated ratios were 2:2:1 respectively (See Figure 2).

OXIDATION OF 1

(a) With Silver Oxide in Methanol.- Hexahydropyridazine (4.0 g, 0.0465 moles) was added dropwise to a cooled (0°C), stirred mixture of silver oxide, (11 g, 0.047 moles) in 42 ml of dry methanol. The reaction was shielded from light with aluminum foil. After all of 1 was added (one hour), the solution was quickly filtered and the solvent rapidly removed under reduced pressure. The residue was rapidly distilled at 25 mm, and the fraction boiling $60-65^{\circ}$ showed only a small azo absorption at $368\text{ m}\mu$ in the ultraviolet region. There was a very large absorption at $232\text{ m}\mu$. No azo band could be seen around 1550 cm^{-1} in the ir and the nmr spectrum was very poor. The fresh product was estimated to be about 30% of 2 and 70% of 3 by ultraviolet spectroscopy.

(b) With Gaseous Oxygen.- A $1.58 \times 10^{-4}\text{M}$ solution of 1 in methanol was prepared and a fine stream of oxygen was bubbled through for approximately one hour. The progress of the reaction was followed in the uv, and the only band that appeared was at $235\text{ m}\mu$, signifying the presence of 3 but not 2.

A $2.64 \times 10^{-3}\text{M}$ solution of 1 in n-hexane was prepared and oxygen bubbled through for one hour, during which time three bands were seen to grow in the ultraviolet. One band at $375\text{ m}\mu$ (azo), one at $240\text{ m}\mu$ ($-\text{C}=\text{N}-$), and a very sharp shoulder at $270\text{ m}\mu$. It is not known what the last peak is due to, but it may be some pyridazine resulting from the further oxidation of 2. Also, in hexane solution, a crop of white needle-like crystals separated out. These were filtered and found to rapidly decompose

with gas evolution at room temperature, leaving behind a yellow oil. A solution of these crystals in methanol or hexane showed a small azo absorption and a large hydrazone absorption in the uv. They were not identified.

(c) With Mercuric Oxide.- Hexahydropyridazine(1) (10.0 g, 0.117 moles) was added slowly with stirring to a cold mixture (0°C) of 27.5 g (0.125 moles) of red mercuric oxide and 27.5 g anhydrous sodium sulfate in 300 ml of n-pentane under an inert atmosphere (N₂). The reaction flask was protected from light with aluminum foil. After the addition was complete (one hour) the mixture was stirred for an additional one hour, after which the pentane was rapidly removed under vacuum. The residue was then immediately distilled at 20 mm through a short column and the fraction boiling at 62-65°C was collected. Solutions of this were then made up with methanol and n-hexane and uv spectra taken. Both solutions showed significant absorptions around 370 mμ, and the product was estimated to be about 85% 2 and 15% 3. On standing at room temperature for several days, the azo absorptions almost completely disappeared, but disappeared much more slowly on storing at 0°C.

The product itself, if kept at room temperature for two hours and then a uv spectrum taken, showed about 70% 2 and 30% 3. On standing for eight hours at room temperature it showed 20% 2 and 80% 3. A solution of the product in methanol could be kept for several days, at 0°C, with little tautomerization taking place.

The nmr spectrum of the freshly prepared product showed what was probably a mixture of 2 and 3 but assignments could not be made def-

initely. An ir spectrum showed no weak band around 1550cm^{-1} , which is where the -N=N- stretching frequency appears, but a broad band around 3300cm^{-1} was seen, indicating N-H absorption.

A mixture of freshly prepared 2 and 3 was injected into a gc column of Ucon on Fluoropak. Only one peak came off, and it was found to consist entirely of 3 from its uv spectrum.

KINETICS

All kinetic runs were done using a Carey Model 14M spectrophotometer with a thermostatted cell compartment. The disappearance of the azo band was followed by setting the instrument at $370\text{ m}\mu$ (for 2) and leaving both the pen and chart on. This resulted in a smooth logarithmic curve being traced by the pen from which values of the absorbance could be read at any particular time.

The temperature of the water flowing through the jacket of the cell compartment was found to be constant within a half of a degree. Opening the cell compartment to insert the sample undoubtedly made the temperature fluctuate by an amount greater than this, and this would affect the kinetics, especially at the beginning of the runs.

The base solution used was prepared by dissolving metallic sodium in anhydrous methanol and was standardized against potassium hydrogen phthalate (Fisher Primary Standard, Lot No. 720978).

Since all runs were performed in the same way, only a general example will be given here.

Determination of Rate Constants.- A solution of the azo compound in methanol was prepared so as to give a fairly strong azo absorption in the uv. The solution was then heated (or cooled), to the temperature at which the run was being made by immersion in the constant temperature bath. A solution of base was also kept at the same temperature. Carefully pipetted aliquots of each solution were then mixed quickly at the reaction temperature, transferred quickly to a 1 cm quartz uv cell and placed in the cell compartment of the spectrophotometer. The transfer time was usually from 4 - 5 seconds, so that very little cooling (or heating) of the solution occurred during the transfer. The spectrometer was immediately switched on (it was set prior to mixing of the solution), and the disappearance of the azo band was followed.

Plots of $2.303 \log (\text{absorbance vs. time (min)})$ were then made and the slopes yielded a constant which when divided by the base concentration gave the first order rate constant for the tautomerization of the azo compound.

REFERENCES

1. O. D. Saltmarsh and R. G. Norrish, J. Chem. Soc., 455(1935)
2. C. E. Bawn and J. Milsted, Trans. Far. Soc., 35, 889(1939)
3. C. T. Genaux and W. D. Walters, J. Am. Chem. Soc., 73, 4497(1951)
4. H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, Proc. Roy. Soc.(London), A218, 416(1953)
5. F. Kern and W. D. Walters, Proc. Nat'l Acad. Sci. U.S., 38, 937(1952)
6. H. M. Frey, Adv. in Phys. Org. Chem., Vol. 4, 147(1966)
7. J. Longrish and H. O. Pritchard, J. Phys. Chem., 62, 761(1958)
8. R. Srinivasan and S. M. Kellner, J. Am. Chem. Soc., 81, 5891(1959)
9. H. R. Gerberich and W. D. Walters, ibid., 83, 4884(1961)
10. M. C. Flowers and H. M. Frey, Proc. Roy. Soc.(London), A257, 122(1960)
11. M. C. Flowers and H. M. Frey, ibid., A2, 424(1961)
12. S. Benson and G. Kistiakowsky, J. Am. Chem. Soc., 64, 80(1942)
13. F. E. Blacet and A. Miller, ibid., 79, 4327(1957)
14. R. Srinivasan, ibid., 81, 1546(1959)
15. R. Srinivasan, Adv. in Photochem., Vol. 1, 83(1963)
16. R. Srinivasan, J. Am. Chem. Soc., 83, 4344(1961)
17. M. C. Flowers and H. M. Frey, J. Chem. Soc., 2758(1960)
18. (a) R. F. Klemm, D. N. Morrison, P. Gilderson and A. T. Blades, Can. J. Chem., 43, 1934(1965)
(b) R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc., 87, 2046(1965)
19. (a) C. H. Wang, S. H. Hsiao, E. Saklad and S. G. Cohen, ibid., 79, 2661(1957)
(b) S. G. Cohen, ibid., 79, 4400(1957)

19. (c) S. G. Cohen and R. Zand, ibid., 84, 586(1962)
20. (a) O. Diels, J. H. Blom and W. Koll, Ann., 443, 242(1925)
(b) O. Diels and K. Alder, Ann., 450, 237(1926)
21. (a) P. Baranger, S. Levisalles and M. Vuidart, Compt. Rend., 236, 1365(1953)
(b) C. G. Overberger and G. Kesslin, J. Org. Chem., 27, 3898(1962)
(c) B. T. Gillis and P. E. Beck, ibid., 27, 1947(1962)
22. R. J. Crawford, A. Mishra and R. J. Dummel, J. Am. Chem. Soc., 88, 3959(1966)
23. (a) C. G. Overberger, J. G. Lombardino, I. Tashlick and R. G. Hiskey, ibid., 79, 2662(1957)
(b) C. G. Overberger and J. G. Lombardino, ibid., 80, 2317(1958)
24. M. Busch and M. Fleischmann, Ber., 43, 740(1910)
25. (a) R. Y. Levina, M. G. Kuz'min and Y. O. S. Shabarov, Doklady Akad. Nauk. S.S.S.R., 121, 303(1958)
(b) R. Y. Levina, M. G. Kuz'min and Y. S. Shabarov, ibid., 127, 111(1959)
(c) R. Y. Levina, M. G. Kuz'min and Y. S. Shabarov, ibid., 129, 600(1959)
(d) R. Y. Levina, Y. S. Shabarov, M. G. Kuz'min, N.I. Vasil'ev, S. I. Pokraka and E. G. Treshchova, Zhur. Obshchei Khim, 29, 3541(1959)
(e) Y. S. Shabarov, R. Y. Levina, M. G. Kuz'min, N. I. Vasil'ev and N. A. Damir, ibid., 30, 3210(1960)
(f) Y. S. Shabarov, N. I. Vasil'ev and R. Y. Levina, ibid., 31, 2482(1961)
(g) M. G. Kuz'min and R. Y. Levina, Doklady Akad. Nauk. S.S.S.R., 135, 879(1960)
26. (a) C. G. Overberger and A. V. DiGiulo, J. Am. Chem. Soc., 80, 6562(1958)
(b) R. L. Hinman, ibid., 79, 414(1957)
(c) C. G. Overberger, I. Tashlick, M. Bernstein and R. G. Hiskey, ibid., 80, 6556(1958)

27. S. G. Beech, J. H. Turnbull and W. Wilson, J. Chem. Soc., 4686(1962)
28. D. E. McGreer, W. Wai and G. Carmichael, Can. J. Chem., 38, 2410(1960)
29. H. Turksma, H. Steinberg and Th. J. DeBoer, Rec. Trav. Chim., 82, 1057(1963)
30. (a) A. Schriesheim and C. Rowe, Jr., J. Am. Chem. Soc., 84, 3160 (1962)
(b) A. Schriesheim and C. Rowe, Tet. Lett., 10, 405(1962)
(c) A. Schriesheim, J. E. Hofmann and C. Rowe, J. Am. Chem. Soc., 83, 3731(1961)
(d) A. Schriesheim, C. Rowe and L. Nasland, ibid., 85, 2111(1963)
(e) S. Bank, C. Rowe and A. Schriesheim, ibid., 85, 2115(1963)
(f) A. Schriesheim, P. Muller and C. Rowe, ibid., 84, 3164(1962)
31. (a) A. Mishra, Ph.D. Thesis, Univ. of Alta., 1965
(b) L. Ali, M.Sc. Thesis, Univ. of Alta., 1967
(c) D. Cameron, Ph.D. Thesis, Univ. of Alta., 1967
(d) G. Erickson, M.Sc. Thesis, Univ. of Alta., 1966

B29879